Long range transport of polybrominated diphenyl ethers (PBDEs) and their natural analogues determined through size-resolved aerosols, and levels in Atlantic Ocean fish from Newfoundland coasts

by

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Abstract

Conventional flame retardants of polybrominated diphenyl ethers (PBDEs) are harmful endocrine disrupters that may endure in the environment and experience long range transport (LRT) to areas far from their sources. Despite a gradual phasing out of PBDEs as flame retardants by the Stockholm Convention and other legislation, humans and the environment are still exposed. Recently, natural methoxy and hydroxyl analogues of PBDEs, MeO-BDEs and OH-BDEs, have been discovered in marine environments and are seasonally associated with phytoplankton primary production that may determine how they contribute to the general persistent organic pollutant (POP) abundance as environmental toxicants. Aerosol mechanisms may link these marine pools to the atmosphere and to the global biosphere by LRT on aerosols. Consumption of biota contaminated with PBDEs and their natural analogues may act as a pathway for human exposure.

The optimization of PBDE and MeO-BDE extraction and analysis is essential to obtain accurate and precise results and improve method efficiency. Approaches to optimize several aspects of PBDE analysis are described here, along with new techniques for aerosol sampling. The efficacy of several novel internal standards for PBDE and MeO-BDE analysis by gas chromatography coupled to mass spectrometry with electron capture negative ionization (GC-ECNI-MS) is assessed. This is achieved through evaluation of standard reference material household dust and Atlantic cod liver with standard addition, internal calibration, and external calibration.

A Micro Orifice Uniform Deposition Impactor (MOUDI) instrument collected aerodynamic aerosol samples in the marine boundary layer. We observe MeO-BDEs in atmospheric aerosols for the first time. We present their atmospheric levels and assessed their sources and potential for LRT based on their aerosol size distribution.

We also examine PBDE and MeO-BDE levels in fish livers from Atlantic cod (*Gadus Morhua*) and Greenland halibut/turbot (*Scophthalmus maximusfish*). These are traditional Newfoundland and Labrador (NL) fishery stocks and are also known to harbor POPs. These fish samples were used to monitor PBDE and MeO-BDE distribution coastal regions of NL.

Acknowledgements

I would like to express my sincere gratitude to the many people who have contributed to my thesis research and allowed for this project to come to fruition. Without these people, I would not have been able to gain this opportunity and for that I am extremely thankful. I would like to first thank my advisor, Dr. Cora J. Young, for taking me under her wing and exposing me to many various aspects of environmental chemistry. She has been an inspirational figure for the past four years that I have known her, and she has guided me through my thesis with her extensive knowledge of atmospheric and analytical chemistry. She has always been encouraging and supportive of my growth as a researcher and I am thankful for her caring and positive presence in my life. I would also like to acknowledge my committee members of Dr. Graham J. Bodwell and Dr. Erika Merschrod for taking their time to learn about my thesis project.

I would like to thank the CJY group and especially its members of Bryan, Teles, John, Katherine, Robert and Trevor for their assistance in sample collection, analysis, and chemistry guidance. Nicole A. Babichuk has been a tremendous help with fish extractions and GC analysis, her help was much appreciated. I would like to thank my friend, Teresa, and my family of Mom, Dad, and my brother Brian for staying with me when I needed it the most. This thesis has been an overall great and wonderful experience.

Save the wolves!

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List of Symbols, Nomenclature, or Abbreviations

°	degree(s)
®	registered trademark
™	trademark
“	inches
∏-∏	pi-pi bonds
µg	microgram
µL	microlitre
µm	micrometre
^{13}C	isotopically labeled carbon atom
A	acetone
ANOVA	analysis of variance
APCI	Atmospheric pressure chemical ionization
APPI	Atmospheric pressure photoionization
ASE	accelerated solvent extraction
BA	bromoanisole
BDE	brominated diphenyl ether
BFR	brominated flame retardant
CCGS	Canadian coast guard fisheries ship
C	Celsius
CDE	chlorobiphenyl
CEPA	Canadian Environmental Protection Act
Chl *a*	chlorophyll *a*
cm	centimetre
Corp.	corporation
DCM	dichloromethane
DDT	dichlorodiphenyltrichloroethane
DE	diatomaceous earth
df	degrees of freedom
DFO	Department of Fisheries and Oceans Canada
DL	detection limit
DOC	dissolved organic carbon
ECNI	electron chemical negative ionization
ECO	eco-friendly, environmentally friendly
e.g.	exempli gratia: for example
EI	electron ionization
EOS	earth observing system
EPA	Environmental Protection Agency
ET	ethyl acetate
et al.	et alia: and others

etc.	et cetera: and so forth
eV	electron volt
ft	feet
GSL	Gulf of St. Lawrence
GSLO	Gulf of St. Lawrence outlet
H	hexane
HEPTA	high-efficiency particulate air
Hi-vol	high volume aerosol sampler
h	hour
hydroxy	OH
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
i.e.	id esf, that is
Inc.	incorporated
IUPAC	international union of pure and applied chemistry
K	Kelvin
kg	kilogram
K_{oa}	octanol-air partition coefficient
K_{ow}	octanol-water partition coefficient
QA	quality assurance
QC	quality control
QFF	quartz fiber filters
g	gram
GC	gas chromatography
GDAS	global data assimilation system
L	litre
LOD	lowest observable detection
LRT	long range transport
m	metre
MAE	microwave assisted extraction
MDL	method detection limit
Me	meth
MeO	methoxy
mg	milligram
min.	minute
mL	millilitre
mm	millimetre
MURASS	Memorial university rooftop atmospheric sampling site
MS	mass spectrometry
m/z	mass to charge ratio
N	north
N/A	not available, not applicable
nano-MOUDI	nano micro orifice uniform deposition impactor

NAPS	National Air Pollution Surveillance
NASA	National Aeronautics and Space Administration
NE	northeast
N.D.	not detected
ng	nanogram
NL	Newfoundland and Labrador
NOAA	National Oceanic and Atmospheric Administration
OA	open Atlantic Ocean
PBDE	polybrominated diphenyl ether
PCB	polychlorobiphenyl
PFDTD	perfluoro-5,8-dimethyl-3,6,9-trioxidodecane
pg	picogram
PM	particulate matter
PM_1	particulate matter: < 1 µm diameter
$PM_{2.5}$	particulate matter: < 2.5 µm diameter
PM_{10}	particulate matter: < 10 µm diameter
POP	persistent organic pollutants
ppm	part per million
psi	pound per square inch
PUF	polyurethane foam
QFF	quartz fiber filter
UAE	ultrasonic-assisted extraction
UV	Ultra violet
rpm	rotations per minute
SE	southeast
sec	second
SFE	supercritical fluid extraction
SIM	selective ionization monitoring
S/N	signal to noise ratio
SML	surface microsurface layer
SPE	solid phase extraction
T_3	triiodothyronine hormone
T_4	thyroxine hormone
T (°C)	temperature in Celsius
T	toluene
TSP	total suspended particulate
VOC	volatile organic carbon
W	west
w.w.	wet weight

List of Appendices

Preface

This thesis is comprised of a series of manuscripts that are in preparation for submission to be published in peer-reviewed scientific journals. Consequently, repetition of introductory and experimental details was expected. All manuscripts were written by Joseph J. Bautista with critical comments provided by Cora J. Young. All research and manuscript preparation were conducted under the guidance of Cora J. Young. In collaboration with Nicole A. Babichuk and Atanu Sarkar, fish samples were prepared and analyzed with the intention of interpreting the data differently from Nicole A. Babichuk's PhD thesis. Her intention is to analyze PBDE concentrations in marine fish and within serum of coastal Newfoundland inhabitants in order to link their cases of hypothyroidism. All results derived from this collaboration had no conflict of interest. The contributions of co-authors are detailed below:

Chapter One: Introduction

Contributions – Prepared by Joseph J. Bautista with editorial comments provided by Cora J. Young

Chapter Two: Sampling, extraction, and separation method development and optimization

Author List – Joseph J. Bautista, Nicole A. Babichuk, Cora J. Young

Contributions – Analyte collection, preparation and analyte extraction experiments were performed by Joseph J. Bautista. GC-MS experiments were

performed by Joseph J. Bautista. ASE preparation and analysis were conducted by Joseph J. Bautista and Nicole A. Babichuk. Data analysis was performed by Joseph J. Bautista with critical comments from Cora J. Young.

Chapter Three: Development of New Calibration Methods for PBDE GC Analysis

Author List – Joseph J. Bautista, Cora J. Young

Contributions – GC-MS experiments and analysis were performed by Joseph J. Bautista. Data analysis was performed by Joseph J. Bautista with critical comments provided by Cora J. Young.

Chapter Four: Analysis of atmospheric aerosol samples

Author List – Joseph J. Bautista, Cora J. Young

Contributions – Sample collection was performed by Joseph J. Bautista and Teles Furlani. MOUDI sample preparation and analysis was performed by Joseph J. Bautista. GC-MS experiments were performed by Joseph J. Bautista. Data interpretation was performed by Joseph J. Bautista with critical comments provided by Cora J. Young.

Chapter Five: Analysis of Atlantic fish samples

Author List – Joseph J. Bautista, Nicole A. Babichuk, Atanu Sarkar, Cora J. Young

Contributions – Sample contributions provided by Laura Wheeland (Centre for Fisheries Ecosystems Research Marine Institute of Memorial University), Hugo Bourdages (DFO), Michel Lebeuf (DFO), and Robert A. Di Lorenzo. Analyte collection, preparation and analyte extraction experiments were performed by

Joseph J. Bautista. GC-MS experiments were performed by Joseph J. Bautista. ASE preparation and analysis were conducted by Joseph J. Bautista and Nicole A. Babichuk. Nicole Babichuk's contributions were facilitated by Atanu Sarkar. Data analysis was performed by Joseph J. Bautista with critical contributions from Cora J. Young.

Chapter Six: Conclusions

Contributions – Prepared by Joseph J. Bautista with editorial comments provided by Cora J. Young.

1 Introduction

1.1 Chemical structures and properties

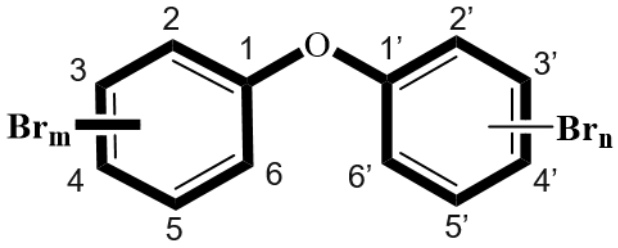

Figure 1-1. International Union of Pure and Applied Chemistry (IUPAC) PBDE structure. Bromine (m = 2 - 6, n = 2' - 6') positioning per aromatic structure[1].

The molecular structure of polybrominated diphenyl ethers (PBDEs, Figure 1-1) consists of two benzene ring structures bonded together by an ether linkage. During PBDE synthesis, these bromine atoms were bonded onto the dual ring structures by electrophilic aromatic substitution reactions with a bromine solvent. Varying degrees of bromine atoms and positions may occupy these ring structures (1 to 10 bound bromines); there are 209 possible PBDE congeners. The International Union of Pure and Applied Chemistry (IUPAC) labelled the PBDEs using the Ballschmiter-Zeller numbering shorthand nomenclature for each bromine atom present. This nomenclature system was similarly applied to chlorine atom numbering in polychlorobiphenyls (PCB) contaminants[2].

PBDEs have relatively high octanol-water partition coefficients (K_{ow}, Equation 1) and octanol-air partition coefficients (K_{oa}, Equation 2). PBDE log K_{ow} values range between 6 to 11, whereas log K_{oa} ranges between 8.8 to 11.4 at 37 °C with values increasing with the degree of bromination[3,4]. This tendency of PBDEs to move to hydrophobic materials from water and atmosphere is attributed to their extreme hydrophobicity. The equilibrium coefficients of K_{ow} and K_{oa} were measured with the concentration of the PBDE

analyte in the octanol phase in contrast to its concentration in water and air, respectively. Unsubstituted diphenyl ethers can act as H-bond acceptors through the lone pair on the ether oxygen and weakly through the ∏ electrons of the aromatic rings. Electron-withdrawing bromine atoms reduce the ∏ electron density on the aromatic ring and prevent H-bonding. Bromine atoms bonded to 2, 2', 6, 6' ring structure positions also prevent hydrogen bond formation with water through dense steric hindrance at the oxygen atom to disrupt water interactions with PBDE[5]. Hence, a greater molecular bromination associated with larger PBDE molecules will be less capable of forming inter-molecular interactions with water. Bromine is a relatively large atom, so water solubility becomes increasingly reduced with every additional hydrophobic bromine substituent.

Equation 1. $K_{ow} = [PBDE]_{octanol} / [PBDE]_{water}$

Equation 2. $K_{oa} = [PBDE]_{octanol} / [PBDE]_{air}$

The ignition of flammable material is associated with a high rate of •OH and •H radical production that will continue to spread with available fuel, oxidizing agent (i.e. molecular oxygen) and continuous heat (~320 to 400 °C)[6,7]. The intention of PBDE as fire retardants was to reduce household burning rate in order to increase the time for occupants to escape. Bromine-carbon bonds within the PBDE molecule begin to thermolyze at ~ 300 to 340 °C, forming free bromine atoms that form stable compounds with radicals generated from burning (i.e. •OH), consequently decreasing overall radical propagation[8]. Brominated flame retardants become more effective with increased bromination; however, the expense of PBDE synthesis becomes more costly with the

degree of bromination[6]. This PBDE ring structure in comparison to brominated aliphatic structures will resist degradation during long term storage and facilitate a slower bromine atom release in order to sustain their use throughout the fire event. Consequently, the structural stability of PBDEs may lengthen their presence in the environment. This stability contributed to their designation as persistent organic pollutants (POPs), among other contaminants such as dichlorodiphenyltrichloroethane (DDT) and PCBs by the Stockholm Convention on POPs, an international United Nations treaty that came into force in 2009[2,9–11].

1.2 Commercial use of PBDE

In the early 1970s, a global mandate was enacted for the use of fire resistant material in consumer products; to comply with these regulations, PBDEs were added to many consumer products[12]. Industrially produced PBDE were categorized by the average number of bromine atoms present per PBDE molecule and designated into categories: penta-BDE, octa-BDE, and deca-BDE. Lower brominated (bromine ≤ 5) PBDE flame retardants make up the penta-BDE mix. These were typically added to flexible polyurethane foam and textile material that were used in manufactured commercial goods such as furniture, domestic appliances, computer cases, among other common indoor household products[11]. The octa-BDE commercial mixture consists of heptabromodiphenyl ether and octa-BDE[13,14]. The most efficient fire retardant, the deca-BDE mix, consists primarily of deca-BDE (i.e. BDE-209) and trace levels of octa-BDE and nona-BDE. Deca-BDE was produced at the largest global volume from 1970 – 2010 and

applied as a coating on electrical parts (e.g. wire, diodes), electronic products, upholstery and drapery fabrics[14–16]. Expensive and environmentally sensitive electronic equipment have utilized high-impact polystyrene components coated with this deca-BDE mix[11]. Since products treated with deca-BDE were coated and not chemically bonded to material surfaces, these PBDEs become readily available for release; these materials can liberate significant PBDE quantities into the environment[17]. Kim *et al.*[18] showed evidence of larger PBDE contamination in close proximity to steel manufacturers and industrial coastal regions[2].

As a response to their detrimental environmental damage, European (2002) and American (2003) regulations on penta-BDE and octa-BDE have progressively phased these products out of market. PBDEs were designated as POPs under the Stockholm Convention in 2008[2,10,11]. Although most global PBDE production has been terminated, deca-BDE legislation in China has allowed for its continued use with legacy PBDEs prevailing within older products and in recycling centers[19,20]. Although Canada considers PBDE exposure as harmful to the environment, seven PBDE groups (tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, octa-BDE, nona-BDE, and deca-BDE) were assessed to not harm human health. According to the Canadian Environmental Protection Act (CEPA, 1999), a substance may be diagnosed as hazardous properties despite the low risk to human health or to the environment depending on the level of exposure. CEPA (1999) persistence and bioaccumulation regulations defined tetra-BDE, penta-BDE, and hexa-

BDE mixes as bioaccumulative compounds stating that all PBDEs are persistent toxicants, therefore can be designated under the Stockholm convention as a POP[21].

1.3 Natural PBDE analogues

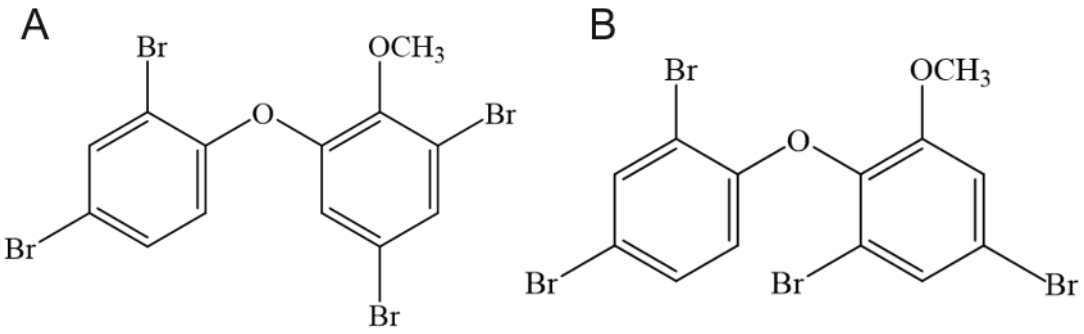

Figure 1-2. Common MeO-BDE structures: (A) 2'-MeO-BDE-68 and (B) 6-MeO-BDE-47.

Natural PBDE analogues have been shown to be produced from sponges, blue mussels, and phytoplankton in oceanic environments. These natural PBDE analogues include methoxy (MeO-) and hydroxy (OH-) functional groups distributed along the carbon ring structure. MeO-BDE congeners 2-(2',4'-dibromophenoxy)-3,5-dibromoanisole (6-MeO-BDE-47) and 2-(2',4'-dibromophenoxy)-4,6-dibromoanisole (2'-MeO-BDE-68) are commonly found in marine environments[22–24] (Figure 1-2). Teuton *et al.*[22] demonstrated that environmental MeO/OH-BDE analogues were primarily natural in origin according to ^{14}C dating with further evidence of MeO-BDE from archived whale oil that pre-dated the manufacturing of industrial PBDE[25,26]. Agarwal *et al.*[27] recently discovered PBDE congeners with unique combinations of both MeO and OH functional groups bonded to the same backbone ring structure, along with other halogens (i.e. iodine and chlorine). This halogenation of MeO/OH-BDEs may lead to more bioactive structures as they

become more hydrophobic and membrane permeable than their parent congeners. These characteristics may attribute to antimicrobial properties in intestinal microflora of multicellular organisms and other marine microorganisms in sediments[24,27–29].

OH/MeO-BDE precursors (e.g. $CHBr_3$ and CH_2Br_2,) and other organic brominated compounds found from the oceanic microsurface layer may be a product of phytoplanktonic chlorophyll and surrounding dissolved organic carbon (DOC). This abundance of brominated phenols, brominated diphenyl ether, bromodioxins, simple organobromine compounds, and associated methyl ethers would suggest the potential to form polybrominated phenoxyanisols structures, specifically MeO-BDE, in blue mussels and sponges[29]. On the other hand, bromoperoxidase present in marine algae can synthesize the main PBDE ring structures of bromophenol and bromocatechol from these bromine intermediates with hydrogen peroxide as a by product. The dimerization of these biosynthesized polybrominated phenols can bring about the formation of OH-BDE by cytochrome P450 within phytoplankton[23,30–34]. Phytoplankton that are currently known to produce natural PBDEs include cyanobacteria (*Apha nizomenon flosaquae, Oscillatoria spongeliae,* and *Nodularia spumigena*) and green macroalgae (*Cladophora fascicularis* and *Cladophora glomerate*). OH-BDE producers include filamentous red algae (*Corallina officinalis*), red macroalgae (*Ceramium tenuicorne*), and brown algae (*Pilayella littoralis*). Precursor molecules (e.g. bromophenol) to MeO/OH-BDE production were shown to be produced by green algae (*Padina arborescens*) and brown algae (*Sargassum siliquatrum* and *Lobophora variegate*)[23,26,31,32,34,35].

Presently, there are no known large-scale industrial sources of MeO-BDE or OH-BDE except as analytical standards synthesized by abiotic surface catalyzed interactions; and as by-products from plastic manufacturing[22,24,31,35–37]. However, these compounds can be formed from reactions of PBDEs. Atmospheric hydroxyl radical interactions with airborne anthropogenic PBDEs can form OH-BDEs[34]. Other abiotic reactions that result in OH-BDE production may occur from the thermal decomposition of brominated fire retardants; or in the presence of sunlight and metal oxides. For example, birnessite (δ-MnO_2) was shown to facilitate the oxidative coupling of 2,4-dibromophenoxy radical and 2,4-dibromo-phenol to produce 2'-OH-BDE-68[35,38,39].

Metabolic conversion (Figure 1-3) from anthropogenic PBDE to OH/MeO-BDE may occur in contaminated marine biota. Selected studies of these toxicant levels that are found in marine biota are presented in chapter 5 (Table 5-2 and Table 5-5). PBDEs may be rapidly ingested and excreted, or gradually metabolized to OH-BDE under excessive PBDE concentrations (ppm level) that will eventually become urinary waste[40,41]. Ingested MeO-BDE were more likely to biotransform to OH-BDE for direct waste disposal by the organism[24,34,36,42–48]. MeO-BDE and OH-BDE congeners could also interchange via enzymatic methylation and demethylation processes in marine fish[23,24,43]. The slower methylation of OH-BDE into MeO-BDE may mask the bioactive phenol group and potentially lead to the bioaccumulation of MeO-BDEs[22–24,40,42]. Although Po *et al.* discovered the only known marine microbial (*I. galbana*) conversion of OH/MeO-BDE from anthropogenic PBDE, they have also submitted, among numerous supporting

evidence, the unlikelihood that industrial PBDE is a precursor to MeO-BDE[24,40,49,50]. The contribution of anthropogenic PBDEs to marine OH/MeO-BDE pools (where these compounds are found at levels of pg/L) is highly implausible unless PBDE concentrations were orders of magnitude greater than OH/MeO-BDE concentrations[40,43,44,46,49]. In reality, PBDEs are commonly found at similar concentrations as OH-BDE and MeO-BDE congeners. There is currently no evidence to indicate any MeO-BDEs or OH-BDEs found in the environment were directly derived from anthropogenic PBDEs.

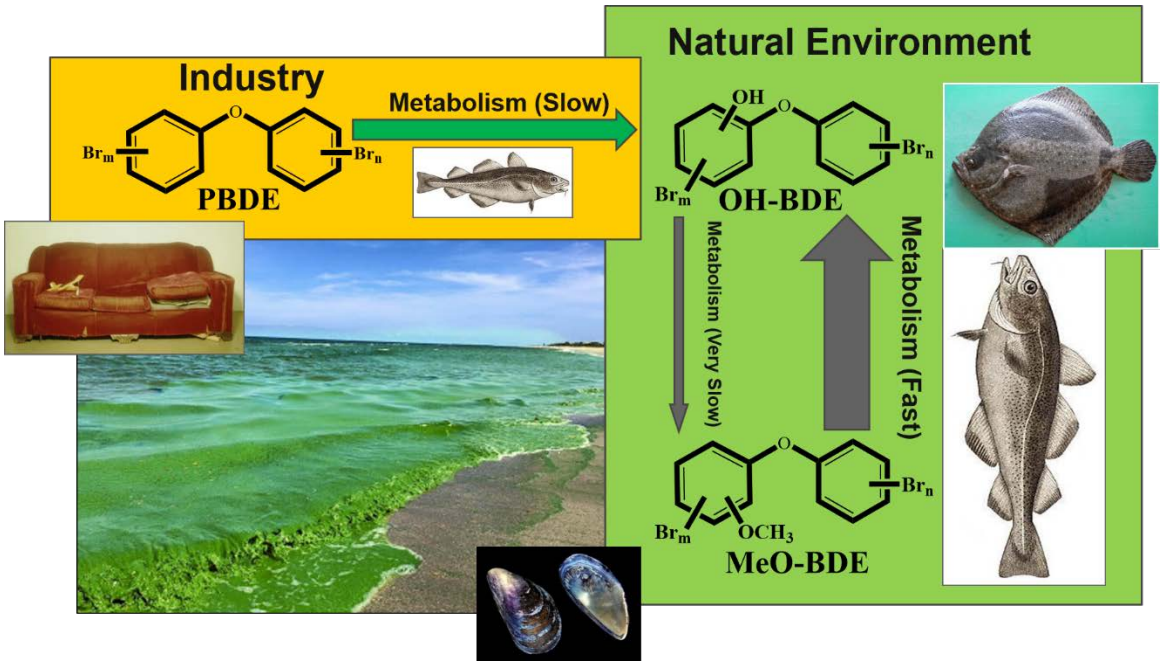

Figure 1-3. Anthropogenic and natural PBDE metabolic pathways.

1.4 Environmental degradation of PBDEs

Atmospheric PBDE decomposition consists of hydroxyl radical interactions, and photolysis[51,52]. Raff, J. D. and Hites, R. A.[53] showed that atmospheric OH-BDE can form from the •OH radical oxidation of PBDE in the presence of light. Under direct sunlight OH-

BDEs in gas phase had ~100 times shorter half-life compared to MeO-BDE and anthropogenic PBDE[54–56]. Conversely, debromination of larger PBDE congeners was the main degradation pathway in terrestrial and marine environments where their lower brominated analogues may be more toxic, bioavailable, and persistent[55,57,58]. This photochemical debromination in the open Atlantic Ocean and Baltic Sea may be less effective in surface waters during the seasonal transition from winter to spring as pelagic waters become more turbulent[59]. At the sediment layer, the main PBDE decomposition is anerobic microbial reduction[60]. Research into PBDE remediation has utilized these anerobic microbial processes to accelerate PBDE breakdown along with oxidation processes from adsorption material (i.e. graphene) and reductive debromination with bimetallic zerovalent iron[61–63].

Uptake in marine biota has comparatively shown that debromination was a major process in the breakdown of larger anthropogenic PBDE[64,65]. Marine biota has been linked to the spread of POPs through their ingestion, the increased PBDE half life within their lipid stores, and the subsequent long-range transport (LRT) through their oceanic migrations. Magali Houde *et al.*[66,67] showed that PBDE contamination was greater for beluga whales in the Canadian St. Lawrence Estuary and ringed seals across the Canadian Arctic. Comparatively small PBDEs (3 to 7 bromine) may be more bioavailable and can more easily bioaccumulate/biomagnify in fish than larger PBDEs due to their associated higher hydrophobicity (BDE-209: log K_{ow} = 9.98)[48,68,69].

1.5 Atmospheric aerosol transport

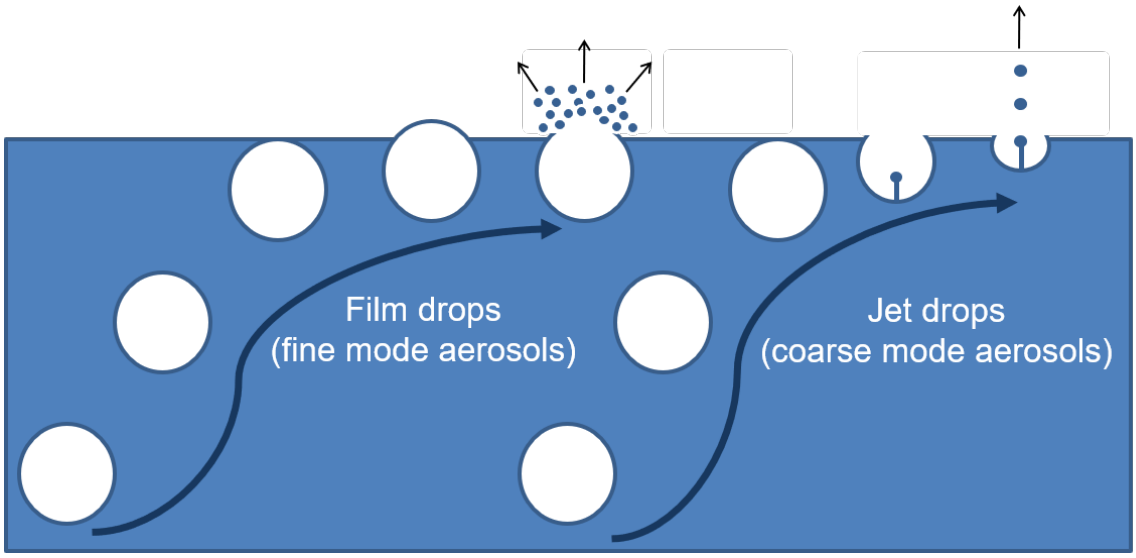

Figure 1-4. Marine aerosol development through film drop and jet drop mechanisms (modified from Lewis *et al.*[70]).

PBDEs have relatively high octanol-air partition coefficients and low vapor pressures that may favor their absorption onto aerosols, thus increasing their potential for LRT[4,71–73]. Aerosols are categorized by their aerodynamic diameter as ultrafine (< 100 nm), fine (100 nm – 1 µm) and coarse (1-10 µm) modes, however aerosol size classifications are often defined differently between studies[74–76]. Aerosol PBDEs can be emitted directly through the use of consumer products[77] and, likely, via marine aerosol emission from the ocean. Marine aerosol formation occurs through film or jet drop mechanisms (Figure 1-4). Film drop aerosols are formed from air bubbles that may contain hydrophobic material collected while they pass through the water column before dispersing on surface water as fine aerosols and the sea-surface microlayer (SSML)[78]. The SSML is a distinct sea surface barrier (10-100 µm depth) between the ocean and the immediate atmosphere known to be enriched in PBDEs[79].

Conversely, jet drop aerosols are produced from the backsplash of waves, rainfall, and general splashing that physically project large water droplets into the air. Wang *et al.*[80], discovered that jet drops could contain organic components. Consequently, marine PBDEs could also contribute to jet drop aerosol composition[80,81]. A small number of aerosols of large diameter (radius: 2 μm to ~0.01 mm) can be created via these means. The relatively large size of jet drop aerosols can result in a short atmospheric lifetime in the order of hours. In contrast, numerous aerosols with relatively small diameters (dry radii < 0.1 μm) could be produced during film drop events. These finer film aerosols have a much longer atmospheric lifetime (days to weeks), thus increasing their potential for LRT. The resultant aerosols that arrive at the surface level could experience coalescing, condensation/dehydration, and degradation that may influence their residence times and interactions with other atmospheric chemicals (e.g. O_3)[79,82,83].

Gas-phase PBDEs can also sorb onto aerosols by gas condensation. The distribution of PBDEs on aerosols of different sizes can allow us to infer sources. Coarse mode aerosols are likely enriched by PBDEs through direct aerosol emissions, whereas gas condensation applies to fine mode aerosol contamination[77]. Fine and ultra-fine aerosols become prime candidates for contaminant absorption due to their associated larger surface areas. Aerosol mass from collected atmospheric samples typically appear to have a bimodal size distribution that represent these fine as well as coarse sized aerosols[75,84–88]. Although current atmospheric PBDE samples are based on the sum of aerosols

collected, innovative size-resolved measurements of PBDEs would lead to a better understanding of PBDE sources.

Generally, POPs released from the ocean, urban, and industrial sources may efficiently and rapidly undergo LRT to distant polar regions (e.g. Arctic) or may be deposited locally through cold condensation[9,73,89,90]. These polar regions act as reservoirs for POPs including PBDEs[91]. Meyer *et al.*[92] discovered BDE-209 within snow cores from the Devon Ice Cap in Nunavut, Canada. Aerosol transport could explain the greater BDE-209 concentrations in relation to other more volatile PBDE congeners. Canadian Arctic air had PBDE concentrations that ranged from 0.83 ± 0.94 pg/m^3 to 0.20 ± 0.15 pg/m^3 [11]. Kim *et al.*[93] observed higher MeO-BDE levels in the atmosphere than the adjacent ocean body, where OH-BDEs dominated[2]. Considering that the ocean is contaminated with anthropogenic PBDE and a source of MeO-BDE, marine aerosols may account for these atmospheric concentrations. The role of aerosols in the LRT of PBDEs remains highly uncertain. The size of aerosols that PBDEs associate with determine their potential for LRT; thus, information about size-resolved aerosol PBDE concentrations could increase our understanding.

1.6 Environmental Concentrations of PBDEs

Selected concentrations of PBDEs in marine water and sediment deposits were presented in Table 1-1 and Table 2-1, respectively. The larger PBDE congeners (e.g. deca-BDE) that have lower water solubility were associated with sediment deposits. Both greater K_{ow} and K_{oa} values and lower mobility correlated with increasing PBDE molecular

size[6,94]. For example, BDE-209 had the lowest solubility at 25 ± ng/L and would readily associate with particulate matter[2]. Conversely, the smaller penta-BDEs were likely associated with the water column and aerosols[95]; total deca-BDE levels range from 4.4 to 77 pg/m^3 [96]. Generally, biota were potentially exposed to PBDEs from various abiotic matrices (e.g. soil and sediment) in close proximity to major commercial product manufacturing sites (i.e. plastics and textiles), urban spaces and recycling plants[68,69].

A large component of the penta-BDE mix, BDE-47 (2,2',4,4'-tetra-BDE), was commonly found in marine environments. BDE-47 has been found in glaucous gull livers (0.5 and 22 µg/kg by w.w.), aquatic invertebrates (2.6 to 118 µg/kg lipid weight), fish liver (7.6 to 307 µg/kg lipid), and many other marine biota. Beluga whales from the St. Lawrence River and Hudson Bay have been shown to contain blubber lipid concentrations of 210 ng/g and 53 ng/g, respectively[44,97]. In the Atlantic ocean, salmon range from 2.6 to 4.8 ng/g lipid weight (medium of 3.8 ng/g) and blue mussels concentrations have been recorded at 0.89 to 1.5 ng/g lipid weight[98]. Larger congeners like BDE-209 was found in ring-billed gull livers at concentrations of 57.2 ± 12.2 ng/g w.w.[68] PBDE and MeO-BDE levels in cod fish and other marine benthic fish are presented in chapter 5 (Table 5-2 and Table 5-5, respectively). Regional contamination and global LRT may be made possible by the migrations of these aforementioned animals[2].

Table 1-1. Selected concentrations of PBDEs in the marine pelagic water column.

Location	Sample Year	∑PBDE	Concentration (pg/L)	Reference
Sachs Harbour, Canadian Arctic	2016	BDEs 2, 8, 15, 30, 28, 49, 47, 100, 99, 154, 153, 183	∑PBDE: 2.26	99
Allen Bay, Canadian Arctic	2016, 2015	BDEs 2, 8, 15, 30, 28, 49, 47, 100, 99, 154, 153, 183	∑PBDE (2016): 9.38, ∑PBDE (2015): 2.93	99
Barrow Strait, Canadian Arctic	2015	BDEs 2, 8, 15, 30, 28, 49, 47, 100, 99, 154, 153, 183	∑PBDE: 13.9	99
Baltic Sea	2013 - 2011	2'-MeO-68, 6-MeO-47	2'-MeO-68: 6.8 ± 59, 6-MeO-47: 19 ± 18	24
East Greenland Sea	2009	BDEs 28, 47, 99, 100, 153, 154, 183, 209	∑PBDE: 0.005 - 0.64 BDE-209: ND - 0.48	100
North/South Atlantic Ocean	2008	BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183	∑PBDE: 0.09 - 0.23	101
East Siberian Sea	2008	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 0.9 – 1.0 (Avg. 1.1), BDE-209: 0.6 - 0.9 (avg. 0.6)	102
Laptev Sea	2008	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 1.0 - 6.2 (Avg. 4.3), BDE-209: 0.6 – 5.5 (Avg. 2.9)	102

Table 1-1 (cont'd). Selected concentrations of PBDEs in the marine pelagic water column.

Location	Sample Year	∑PBDE	Concentration (pg/L)	Reference
Kara Sea	2008	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 1.3, BDE-209: 0.7	[102]
East of Greenland	2005	BDEs 17, 28, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190, 209	∑PBDE: 0.9 - 1.5 (Avg. 1.2), BDE-209: 0.3 (avg. 0.3)	[102]
Chukchi Sea	2005	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 1.1 - 2.4 (Avg. 1.8), BDE-209: 0.1 - 1.5 (Avg. 0.8)	[102]
Beaufort Sea	2005	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 3.9 - 5.9 (Avg. 4.9), BDE-209: 2.1 - 4.1 (Avg. 3.1)	[102]
Kara Sea	2005, 2003	BDEs 7, 8/11, 10, 12/13, 15, 17/25, 28/33, 30, 32, 35, 37, 47, 49, 51, 66, 71, 75, 77, 79, 85, 99, 100, 105, 116, 119/120, 126, 128, 138/166, 140, 153, 154, 155, 181, 183, 190, 203	∑PBDE: 1.8 - 10.8	[103]
Barents Sea	2001	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 0.9 - 8.3 (Avg. 3.0), BDE-209: 0.6 - 7.8 (Avg. 2.6)	[102]
Norwegian Sea	2001	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 1.9 - 11.2 (Avg. 6.6), BDE-209: 1.5 – 10.4 (Avg. 6.0)	[102]
Central Arctic Ocean Basin	2001	BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	∑PBDE: 0.2 -4.2 (Avg. 1.2), BDE-209: 0.2 - 3.4 (Avg. 0.9)	[102]

Table 1-2. Selected concentrations of PBDEs in marine sediments.

Location	Sample Year	∑PBDE	Concentration (pg/g)	Reference
German Bight	2013, 2012	BDEs 28, 47, 66, 99, 100, 153, 154, 183	Avg. 62 ± 61	[104]
Scheldt estuary, Netherlands/Belgium	2010	BDEs 28, 47, 99, 100, 153, 154, 183, 209	∑PBDE: 0.1, BDE-209: 0.43-1200	[105]
Western Arctic Ocean	2008	BDEs 47, 99, 100, 153, 154, 183, 138, 209	∑PBDE: 0.004 - 0.149, BDE-209: ND - 0.805	[106]
Gulf of Lion, France	2005	BDEs 17, 28, 71, 47, 66, 99, 85, 100, 153, 154, 138, 183, 190, 209	∑PBDE: ND - 2.60, BDE-209: 0.06 - 140	[107]
Spanish coast, Spain	2002	BDEs 28, 33, 47, 66, 77, 100, 99, 118, 154, 153, 183, 209	∑PBDE: 0.24 - 3.94, BDE-209: 2.62 - 132	[108]
Scheldt estuary, the Netherlands	2001	BDEs 28, 47, 66, 85, 99, 100, 138, 153, 154, 209	∑PBDE: 14 - 22, BDE-209: 240 – 1650	[109]

*ND = not detected

1.7 Human exposure

Environmental exposure to PBDEs can occur through dermal absorption, ingestion, and inhalation mechanisms[110]. Relatively high rates of PBDE absorption through skin tissues may occur during industrial manufacturing, PBDE research in laboratories, and exposure to consumer goods (e.g. old furniture)[111]. Nonetheless, PBDE exposure through consumption and respiration may inherently introduce a greater PBDE content into mammalian systems. Gas phase PBDE or ambient PBDEs sorbed to dust particles may be inhaled directly into humans and other vertebrate organisms. Aerosols with aerodynamic diameters less than 2.5 μm were likely to absorb into the blood stream via the alveoli in

the lungs[112]. Therefore, aerosol size may determine their source, atmospheric fate, and potential to impact human health.

Consumption of fish, meat, dairy products and poultry are possible major sources of PBDE contaminant exposure[76]. Elevated PBDE levels in fish may contribute to human exposure to anthropogenic PBDE and naturally occurring MeO/OH-BDE congeners[2,69,113]. Metabolism of ingested PBDEs will likely result in the breakdown of larger PBDEs (7 to 10 bromine) to smaller congeners (1 to 6 bromine)[111]. Upon lengthier residence time within the body, PBDE metabolites could partition to lipids and cellular membranes that become susceptible to bioaccumulation and biomagnification effects. PBDEs with log K_{ow} greater than 5 may bioaccumulate. However, extremely hydrophobic PBDEs (K_{ow} > log 9.5) have a lower bioavailability and bioaccumulation rate, which may lead to excretion through urine. Human PBDE bioaccumulation effects were likely to have the potential to be more detrimental to people with compromised immune systems and babies who are fed their mother's milk[114–116]. Child bioaccumulation effects may be 2 to 5-fold greater than those of parents due to their adolescent behavior that can include playing on the floor and putting objects in their mouths[110,117].

1.8 PBDE toxicity to humans

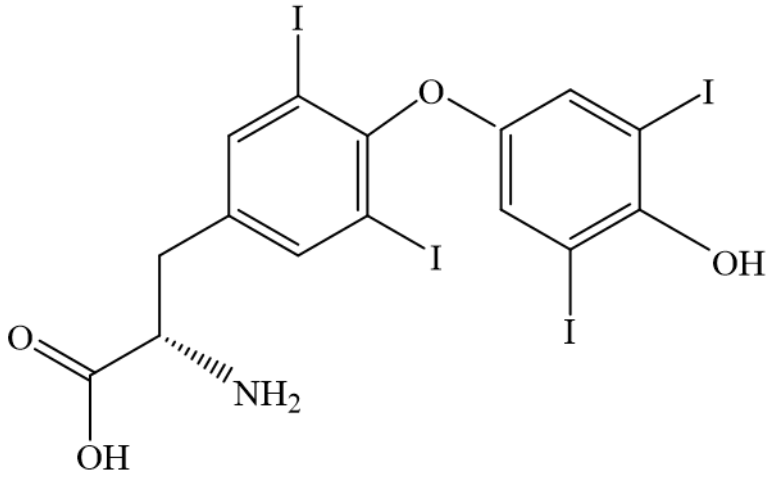

Figure 1-5. Thyroid hormone thyroxine (T_4) structure.

Anthropogenic PBDEs and their naturally occurring analogues of methoxy substituted (MeO-BDE) and hydroxy-substituted (OH-BDE) PBDEs are thyroid hormone analogues to thyroxine (T_4, Figure 1-5) and triiodothyronine (T_3). These PBDEs compete for binding sites responsible for oxidative phosphorylation, thyroid hormone transporting proteins, transthyretin, and thyroid binding globulin. Due to OH-BDE's bioactive hydroxy functional group, these congeners are the most potent competitors[32,118,119]. An epidemiological study conducted by Meerts *et al.*[120] showed evidence of neurological and reproductive issues specifically relating to the kidney, thyroid and liver with exposure. These MeO/OH-BDE congeners have been found to suppress androgenic pathways through receptor inhibition. The inhalation of PBDE congeners can encourage apoptosis in astrocytoma cells in a similar fashion[112,121].

1.9 Project objectives and rationale

The primary aim of this work was to monitor anthropogenic PBDE and natural MeO/OH-BDE toxicants in environmental media to determine their potential for global exposure and the mechanism of LRT. To do this, adequate analytical methods needed to be developed for these samples. Developing these analytical methods was the secondary goal of this work. The two goals were accomplished in four parts: (1) method development of environmental sampling based on size-resolved aerosols, analyte liquid/liquid extraction with solvent extraction techniques, and gas chromatography coupled to mass spectrometry analysis (Chapter 2); (2) selection of optimal internal standards for atmospheric aerosol and fish samples through comparison to standard addition and validated with environmental samples (Chapter 3); (3) measurement of PBDE and MeO-BDE analytes in outdoor size-resolved aerosol samples from a polluted marine environment (Chapter 4); and (4) measurement of PBDE and MeO-BDE analytes in fish liver samples from around Newfoundland island (Chapter 5).

1.10 References

(1) Rydén, A. *Synthesis of Organobromines as a Tool for Their Characterisation and Environmental Occurrence Assessment*; 2013.

(2) Vonderheide, A. P.; Mueller, K. E.; Meija, J.; Welsh, G. L. Polybrominated Diphenyl Ethers: Causes for Concern and Knowledge Gaps Regarding Environmental Distribution, Fate and Toxicity. *Sci. Total Environ.* **2008**, *400* (1), 425–436.

(3) Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Gobas, F. A. P. C. Bioaccumulation Behaviour of Polybrominated Diphenyl Ethers (PBDEs) in a Canadian Arctic Marine Food Web. *Sci. Total Environ.* **2008**, *401* (1–3), 60–72. https://doi.org/http://dx.doi.org/10.1016/j.scitotenv.2008.03.045.

(4) Harner, T.; Shoeib, M. Measurements of Octanol-Air Partition Coefficients (Koa) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. *J. Chem. Eng. Data* **2002**, *47*, 228–232. https://doi.org/10.1021/je010192t.

(5) Long, J.; Youli, Q.; Yu, L. Effect Analysis of Quantum Chemical Descriptors and Substituent Characteristics on Henry's Law Constants of Polybrominated Diphenyl Ethers at Different Temperatures. *Ecotoxicol. Environ. Saf.* **2017**, *145* (July), 176–183. https://doi.org/10.1016/j.ecoenv.2017.07.024.

(6) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. Polybrominated Diphenyl Ether (PBDE) Flame Retardants. *Sci. Total Environ.* **2001**, *275* (1–3), 1–17. https://doi.org/Doi: 10.1016/s0048-9697(01)00852-x.

(7) Sullivan, A. L.; Ellis, P. F.; Knight, I. K. A Review of Radiant Heat Flux Models Used in Bushfire Applications. *Int. J. Wildl. Fire* **2003**, *12* (1), 101. https://doi.org/10.1071/WF02052.

(8) Agency, U. S. E. P. *Technical Fact Sheet - Polybrominated Diphenyl Ethers (PBDE)*; 2017.

(9) Secretariat of the Stockholm Convention on Persistent Organic Pollutants United Nations Environment Programme (UNEP) Chemicals International Environment House. *Ridding the World of POPs: A Guide to the Stockholm Convention*; United Nations Environment Programme: Châtelaine, Geneva, Switzerland, 2005.

(10) Birnbaum, L. S.; Cohen Huba, E. A. Polybrominated Diphenyl Ethers: A Case Study for Using Biomonitoring Data to Address Risk Assessment Questions. *Environ. Health Perspect.* **2006**, *114* (11), 1770–1775. https://doi.org/10.1289/ehp.9061.

(11) Li, Y.-F.; Qiao, L.-N.; Ren, N.-Q.; Sverko, E.; Mackay, D.; Macdonald, R. W. Decabrominated Diphenyl Ethers (BDE-209) in Chinese and Global Air: Levels, Gas/Particle Partitioning, and Long-Range Transport: Is Long-Range Transport of BDE-209 Really Governed by the Movement of Particles? *Environ. Sci. Technol.* **2017**, *51* (2), 1035–1042. https://doi.org/10.1021/acs.est.6b05395.

(12) Venier, M.; Salamova, A.; Hites, R. A. Halogenated Flame Retardants in the Great Lakes Environment. *Acc. Chem. Res.* **2015**, *48* (7), 1853–1861. https://doi.org/10.1021/acs.accounts.5b00180.

(13) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-Retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254. https://doi.org/10.1021/es060630m.

(14) Di Carlo, F. J.; Seifter, J.; DeCarlo, V. J. Assessment of the Hazards of Polybrominated Biphenyls. *Environ. Health Perspect.* **1978**, *23*, 351–365.

(15) Alexander, J.; Benford, D.; Boobis, A. R.; Ceccatelli, S.; Cottrill, B.; Cravedi, J.-P.; Di Domenico, A.; Doerge, D.; Dogliotti, D.; Edler, L.; Farmer, P.; Filipič, M.; Fink-Gremmels, J.; Fürst, P.; Guérin, T.; Knutsen, H. K.; Machala, M.; Mutti, A.; Rose, R. Scientific Opinion on Polybrominated Diphenyl Ethers (PBDEs) in Food. *EFSA J.* **2011**, *9* (5), 1–274. https://doi.org/10.2903/j.efsa.2011.2156.

(16) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated Flame Retardants in the Arctic Environment - Trends and New Candidates. *Sci. Total Environ.* **2010**, *408* (15), 2885–2918. https://doi.org/10.1016/j.scitotenv.2009.08.037.

(17) Wang, D.; Cai, Z.; Jiang, G.; Leung, A.; Wong, M. H.; Wai, K. W. Determination of Polybrominated Diphenyl Ethers in Soil and Sediment from an Electronic Waste Recycling Facility. *Chemosphere* **2005**, *60* (6), 810–816. https://doi.org/10.1016/j.chemosphere.2005.04.025.

(18) Kim, Y. H.; Kim, H. S.; Choi, H. G.; Cho, H. S.; Moon, H. B. Contamination and Bioaccumulation of Polybrominated Diphenyl Ethers (PBDEs) in Gwangyang Bay, Korea. *Toxicol. Environ. Health Sci.* **2012**, *4* (1), 42–49. https://doi.org/10.1007/s13530-012-0116-7.

(19) Ni, K.; Lu, Y.; Wang, T.; Shi, Y.; Kannan, K.; Xu, L.; Li, Q.; Liu, S. Polybrominated Diphenyl Ethers (PBDEs) in China: Policies and Recommendations for Sound Management of Plastics from Electronic Wastes. *J. Environ. Manage.* **2013**, *115*, 114–123. https://doi.org/10.1016/j.jenvman.2012.09.031.

(20) Malkoske, T.; Tang, Y.; Xu, W.; Yu, S. Brominated Flame Retardants (BFRs) in China : Wastewater Sources and Treatment Methods. **2016**, *4*, 2014–2017.

(21) W.A. Johnston, F.J. Nicholson, A. R. and G. D. S. *FAO FISHERIES TECHNICAL PAPER - 340*; FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS: Torry, Aberdeen, Scotland, UK, 1994. https://doi.org/M-47.

(22) Teuten, E. L.; Xu, L.; Reddy, C. M. Two Abundant Bioaccumulated Halogenated Compounds Are Natural Products. *Science* **2005**, *307*, 917–920. https://doi.org/10.1126/science.1106882.

(23) Bidleman, T. F.; Agosta, K.; Andersson, A.; Haglund, P.; Liljelind, P.; Hegmans, A.; Jantunen, L. M.; Nygren, O.; Poole, J.; Ripszam, M.; et al. Sea-Air Exchange of Bromoanisoles and Methoxylated Bromodiphenyl Ethers in the Northern Baltic. *Mar. Pollut. Bull.* **2016**, *112* (1–2), 58–64. https://doi.org/10.1016/j.marpolbul.2016.08.042.

(24) Wiseman, S. B.; Wan, Y.; Chang, H.; Zhang, X.; Hecker, M.; Jones, P. D.; Giesy, J. P. Polybrominated Diphenyl Ethers and Their Hydroxylated/Methoxylated Analogs: Environmental Sources, Metabolic Relationships, and Relative Toxicities. *6th Int. Conf. Mar. Pollut. Ecotoxicol.* **2011**, *63* (5–12), 179–188. https://doi.org/http://dx.doi.org/10.1016/j.marpolbul.2011.02.008.

(25) Teuten, E. L.; Reddy, C. M. Halogenated Organic Compounds in Archived Whale Oil: A Pre-Industrial Record. *Environ. Pollut.* **2007**, *145* (3), 668–671. https://doi.org/10.1016/j.envpol.2006.08.022.

(26) Malmvärn, A.; Zebühr, Y.; Kautsky, L.; Bergman, Å.˚; Asplund, L. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers and Polybrominated Dibenzo-p-Dioxins in Red Alga and Cyanobacteria Living in the Baltic Sea. *Chemosphere* **2008**, *72* (6), 910–916. https://doi.org/10.1016/j.chemosphere.2008.03.036.

(27) Agarwal, V.; Li, J.; Rahman, I.; Borgen, M.; Aluwihare, L. I.; Biggs, J. S.; Paul, V. J.; Moore, B. S. Complexity of Naturally Produced Polybrominated Diphenyl Ethers Revealed via Mass Spectrometry. *Environ. Sci. Technol.* **2015**, *49* (3), 1339–1346.

(28) Fu, X.; Schmitz, F. J.; Abbas, S. A.; Govindan, M.; Hanson, K. M.; Horton, P. A.; Crews, P.; Laney, M.; Schatzman, R. C. Enzyme Inhibitors: New and Known Polybrominated Phenols and Diphenyl Ethers from Four Indo-Pacific Dysidea Sponges. *J. Nat. Prod.* **1995**, *58* (9), 1384–1391. https://doi.org/10.1021/np50123a008.

(29) Sinkkonen, S.; Rantalainen, A.-L.; Paasivirta, J.; Lahtiperä, M. Polybrominated Methoxy Diphenyl Ethers (MeO-PBDEs) in Fish and Guillemot of Baltic, Atlantic and Arctic Environments. *Chemosphere* **2004**, *56* (8), 767–775. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2004.02.007.

(30) Agarwal, V.; El Gamal, A. A.; Yamanaka, K.; Poth, D.; Kersten, R. D.; Schorn, M.; Allen, E. E.; Moore, B. S. Biosynthesis of Polybrominated Aromatic Organic Compounds by Marine Bacteria. *Nat. Chem. Biol.* **2014**, *10* (8), 640–647. https://doi.org/10.1038/nchembio.1564.

(31) Lin, K.; Gan, J.; Liu, W. Production of Hydroxylated Polybrominated Diphenyl Ethers from Bromophenols by Bromoperoxidase-Catalyzed Dimerization. *Environ. Sci. Technol.* **2014**, *48* (20), 11977–11983. https://doi.org/10.1021/es502854e.

(32) Dahlberg, A.-K.; Lindberg Chen, V.; Larsson, K.; Bergman, Å.; Asplund, L. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in Long-Tailed Ducks (Clangula Hyemalis) and Their Main Food, Baltic Blue Mussels (Mytilus Trossulus × Mytilus Edulis). *Chemosphere* **2016**, *144*, 1475–1483. https://doi.org/10.1016/j.chemosphere.2015.10.012.

(33) Lin, C. Y.; Manley, S. L. Bromoform Production from Seawater Treated with Bromoperoxidase. *Limnol. Oceanogr.* **2012**, *57* (6), 1857–1866. https://doi.org/10.4319/lo.2012.57.06.1857.

(34) Löfstrand, K.; Liu, X.; Lindqvist, D.; Jensen, S.; Asplund, L. Seasonal Variations of Hydroxylated and Methoxylated Brominated Diphenyl Ethers in Blue Mussels from the Baltic Sea. *Chemosphere* **2011**, *84* (4), 527–532. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2011.01.001.

(35) Lin, K.; Yan, C.; Gan, J. Production of Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) from Bromophenols by Manganese Dioxide. **2014**, *48* (1), 263–271.

(36) Zhang, K.; Wan, Y.; Jones, P. D.; Wiseman, S.; Giesy, J. P.; Hu, J. Occurrences and Fates of Hydroxylated Polybrominated Diphenyl Ethers in Marine Sediments in Relation to Trophodynamics. *Environ. Sci. Technol.* **2012**, *46* (4), 2148–2155. https://doi.org/10.1021/es203195s.

(37) Ren, M.; Zeng, H.; Peng, P. A.; Li, H. R.; Tang, C. M.; Hu, J. F. Brominated Dioxins/Furans and Hydroxylated Polybrominated Diphenyl Ethers: Occurrences in Commercial 1,2-Bis(2,4,6-Tribromophenoxy)Ethane (BTBPE) and 2,4,6-Tribromophenol, and Formation during Synthesis of BTBPE. *Environ. Pollut.* **2017**, *226*, 394–403. https://doi.org/10.1016/j.envpol.2017.03.077.

(38) Roszko, M.; Szymczyk, K.; Rzepkowska, M.; Jędrzejczak, R. Preliminary Study on Brominated Dioxins/Furans and Hydroxylated/Methoxylated PBDEs in Baltic Cod (Gadus Morhua) Liver. Comparison to the Levels of Analogue Chlorinated Co-Occurring Pollutants. *Mar. Pollut. Bull.* **2015**, *96* (1–2), 165–175. https://doi.org/10.1016/j.marpolbul.2015.05.032.

(39) Liu, H.; Zhao, H.; Quan, X.; Zhang, Y.; Chen, S.; Zhao, H. Formation of 2'-Hydroxy-2,3,4,5-Tetrabromodipheyl Ether (2-HO-BDE68) from 2,4-Dibromophenol in Aqueous Solution under Simulated Sunlight Irradiation. *Chemosphere* **2011**, *84* (4), 512–518. https://doi.org/10.1016/j.chemosphere.2011.03.011.

(40) Wan, Y.; Wiseman, S.; Chang, H.; Zhang, X.; Jones, P. D.; Hecker, M.; Kannan, K.; Tanabe, S.; Hu, J.; Lam, M. H. W. Origin of Hydroxylated Brominated Diphenyl Ethers: Natural Compounds or Man-Made Flame Retardants? *Environ. Sci. Technol.* **2009**, *43* (19), 7536–7542.

(41) Stapleton, H. M.; Kelly, S. M.; Pei, R.; Letcher, R. J.; Gunsch, C. Metabolism of Polybrominated Diphenyl Ethers (PBDEs) by Human Hepatocytes in Vitro. *Environ. Health Perspect.* **2009**, *117* (2), 197–202. https://doi.org/10.1289/ehp.11807.

(42) Liu, F.; Wiseman, S.; Wan, Y.; Doering, J. A.; Hecker, M.; Lam, M. H. W.; Giesy, J. P. Multi-Species Comparison of the Mechanism of Biotransformation of MeO-BDEs to OH-BDEs in Fish. *Aquat. Toxicol.* **2012**, *114–115*, 182–188. https://doi.org/http://dx.doi.org/10.1016/j.aquatox.2012.02.024.

(43) Hakk, H.; Letcher, R. J. Metabolism in the Toxicokinetics and Fate of Brominated Flame Retardants - A Review. *Environ. Int.* **2003**, *29* (6), 801–828. https://doi.org/10.1016/S0160-4120(03)00109-0.

(44) Wan, Y.; Liu, F.; Wiseman, S.; Zhang, X.; Chang, H.; Hecker, M.; Jones, P. D.; Lam, M. H. W.; Giesy, J. P. Interconversion of Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in Japanese Medaka. *Environ. Sci. Technol.* **2010**, *44* (22), 8729–8735. https://doi.org/10.1021/es102287q.

(45) Zhang, K.; Wan, Y.; Giesy, J. P.; Lam, M. H. W.; Wiseman, S.; Jones, P. D.; Hu, J. Tissue Concentrations of Polybrominated Compounds in Chinese Sturgeon (Acipenser Sinensis): Origin, Hepatic Sequestration, and Maternal Transfer. *Environ. Sci. Technol.* **2010**, *44* (15), 5781–5786. https://doi.org/10.1021/es100348g.

(46) Feng, C.; Xu, Y.; Zha, J.; Luo, Q.; Shan, X.; Wang, Z. Toxicokinetics and the Related Metabolites in Rainbow Trout (Oncorhynchus Mykiss) after Exposure to Decabromodiphenyl Ether. *Sci. China Chem.* **2010**, *53* (11), 2379–2386. https://doi.org/10.1007/s11426-010-4020-1.

(47) Kim, U.-J.; Jo, H.; Lee, I.-S.; Joo, G.-J.; Oh, J.-E. Investigation of Bioaccumulation and Biotransformation of Polybrominated Diphenyl Ethers, Hydroxylated and Methoxylated Derivatives in Varying Trophic Level Freshwater Fishes. *Chemosphere* **2015**, *137*, 108–114. https://doi.org/10.1016/j.chemosphere.2015.05.104.

(48) Lee, H. J.; Kim, G. B. An Overview of Polybrominated Diphenyl Ethers (PBDEs) in the Marine Environment. **2015**, *50* (July 2008), 119–142.

(49) Po, B. H. K.; Ho, K.-L.; Lam, M. H. W.; Giesy, J. P.; Chiu, J. M. Y. Uptake and Biotransformation of 2,2′,4,4′-Tetrabromodiphenyl Ether (BDE-47) in Four Marine Microalgae Species. *Sci. Rep.* **2017**, *7* (March), 44263. https://doi.org/10.1038/srep44263.

(50) Haglund, P. S.; Zook, D. R.; Buser, H. R.; Hu, J. Identification and Quantification of Polybrominated Diphenyl Ethers and Methoxy-Polybrominated Diphenyl Ethers in Baltic Biota. *Environ. Sci. Technol.* **1998**, *31* (11), 3281–3287. https://doi.org/10.1039/b412924p.

(51) Wang, L.; Tang, L.; Wang, R.; Wang, X.; Ye, J. . L. Y. Biosorption and Degradation of Decabromodiphenyl Ether by Brevibacillus Brevis and the Influence of Decabromodiphenyl Ether on Cellular Metabolic Responses. *Environ. Sci. Pollut. Res.* **2015**, *23* (6), 5166–5178.

(52) Mulder, M. D.; Heil, A.; Kukučka, P.; Kuta, J.; Přibylová, P.; Prokeš, R.; Lammel, G. Long-Range Atmospheric Transport of PAHs, PCBs and PBDEs to the Central and Eastern Mediterranean and Changes of PCB and PBDE Congener Patterns in Summer 2010. *Atmos. Environ.* **2015**, *111* (0), 51–59. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2015.03.044.

(53) Raff, J. D., Hites, R. A. Gas-Phase Reactions of Brominated Diphenyl Ethers with OH Radicals. *J. Phys. Chem. A* **2006**, *110* (37), 10783−10792.

(54) Pan, Y.; Tsang, D. C. W.; Wang, Y.; Li, Y.; Yang, X. The Photodegradation of Polybrominated Diphenyl Ethers (PBDEs) in Various Environmental Matrices: Kinetics and Mechanisms. *Chem. Eng. J.* **2016**, *297*, 74–96. https://doi.org/10.1016/j.cej.2016.03.122.

(55) Eriksson, J.; Green, N.; Marsh, G.; Bergman, Å.̊. Photochemical Decomposition of 15 Polybrominated Diphenyl Ether Congeners in Methanol/Water. *Environ. Sci. Technol.* **2004**, *38* (11), 3119–3125. https://doi.org/10.1021/es049830t.

(56) Xue, W.; Chen, J.; Xie, Q. Direct and Dissolved Oxygen Involved Photodegradation of MeO-PBDEs in Water. *J. Hazard. Mater.* **2016**, *307*, 344–349. https://doi.org/10.1016/j.jhazmat.2016.01.016.

(57) Söderström, G.; Sellström, U.; De Wit, C. A.; Tysklind, M. Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). *Environ. Sci. Technol.* **2004**, *38* (1), 127–132. https://doi.org/10.1021/es034682c.

(58) Jianxian, S.; Hui, P.; Jianying, H. Temporal Trends of Polychlorinated Biphenyls, Polybrominated Diphenyl Ethers, and Perfluorinated Compounds in Chinese Sturgeon (*Acipenser Sinensis*) Eggs (1984–2008). *Environ. Sci. Technol.* **2015**, *49* (3), 1621–1630. https://doi.org/10.1021/es505378b.

(59) Kuivikko, M.; Kotiaho, T.; Hartonen, K.; Tanskanen, A.; Vähätalo, A. V. Modeled Direct Photolytic Decomposition of Polybrominated Diphenyl Ethers in the Baltic Sea and the Atlantic Ocean. *Environ. Sci. Technol.* **2007**, *41* (20), 7016–7021. https://doi.org/10.1021/es070422+.

(60) Tokarz, J. A.; Ahn, M.-Y.; Leng, J.; Filley, T. R.; Nies, L. Reductive Debromination of Polybrominated Diphenyl Ethers in Anaerobic Sediment and a Biomimetic System. *Environ. Sci. Technol.* **2008**, *42* (4), 1157–1164. https://doi.org/10.1021/es071989t.

(61) Gerecke, A. C., Hartmann, P. C., Heeb, N. V., Kohler H-P. E., Giger, W., Schmid, P., Zennegg, M., Kohler, M. Anaerobic Degradation of Decabromodiphenyl Ether. *Environ. Sci. Technol.* **2005**, *39* (4), 1078–1083.

(62) Zhuang, Y.; Jin, L.; Luthy, R. G. Kinetics and Pathways for the Debromination of Polybrominated Diphenyl Ethers by Bimetallic and Nanoscale Zerovalent Iron: Effects of Particle Properties and Catalyst. *Chemosphere* **2012**, *89* (4), 426–432. https://doi.org/10.1016/j.chemosphere.2012.05.078.

(63) Li, L.; Hu, J.; Shi, X.; Ruan, W.; Luo, J.; Wei, X. Theoretical Studies on Structures, Properties and Dominant Debromination Pathways for Selected Polybrominated Diphenyl Ethers. *Int. J. Mol. Sci.* **2016**, *17* (6), 927. https://doi.org/10.3390/ijms17060927.

(64) Mizukawa, K.; Yamada, T.; Matsuo, H.; Takeuchi, I.; Tsuchiya, K.; Takada, H. Biomagnification and Debromination of Polybrominated Diphenyl Ethers in a Coastal Ecosystem in Tokyo Bay. *Sci. Total Environ.* **2013**, *449*, 401–409. https://doi.org/10.1016/j.scitotenv.2013.01.092.

(65) Kelly, B. C.; Blair, J. D.; Gobas, F. A. P. C.; Ikonomou, M. G. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in a Canadian Arctic Marine Food Web. *Environ. Sci. Technol.* **2008**, *42* (19), 7069–7077. https://doi.org/10.1021/es801275d.

(66) Simond, A. E.; Houde, M.; Lesage, V.; Verreault, J. Temporal Trends of PBDEs and Emerging Flame Retardants in Belugas from the St. Lawrence Estuary (Canada) and Comparisons with Minke Whales and Canadian Arctic Belugas. *Environ. Res.* **2017**, *156* (November 2016), 494–504. https://doi.org/10.1016/j.envres.2017.03.058.

(67) Houde, M.; Wang, X.; Ferguson, S. H.; Gagnon, P.; Brown, T. M.; Tanabe, S.; Kunito, T.; Kwan, M.; Muir, D. C. G. Spatial and Temporal Trends of Alternative Flame Retardants and Polybrominated Diphenyl Ethers in Ringed Seals (Phoca Hispida) across the Canadian Arctic. *Environ. Pollut.* **2017**, 1–11. https://doi.org/10.1016/j.envpol.2017.01.023.

(68) Gentes, M. L.; Letcher, R. J.; Caron-Beaudoin, É.; Verreault, J. Novel Flame Retardants in Urban-Feeding Ring-Billed Gulls from the St. Lawrence River, Canada. *Environ. Sci. Technol.* **2012**, *46* (17), 9735–9744. https://doi.org/10.1021/es302099f.

(69) Watanabe, I.; Sakai, S. Environmental Release and Behavior of Brominated Flame Retardants. *Environ. Int.* **2003**, *29* (6), 665–682. https://doi.org/10.1016/s0160-4120(03)00123-5.

(70) Lewis, E. R.; Stephen E.; Schwartz, S. E. *Sea Salt Aerosol Production: Mechanisms, Methods, Measurements, and Models*; 2004.

(71) Tittlemier, S. A.; Tomy, G. T. Vapor Pressures of Six Brominated Diphenyl Ether Congeners. *Environ. Toxicol. Chem.* **2009**, *20* (1), 146–148.

(72) Wong, A.; Lei, Y. D.; Alaee, M.; Wania, F. Vapor Pressures of the Polybrominated Diphenyl Ethers. *J. Chem. Eng. Data* **2001**, *46* (2), 239–242. https://doi.org/10.1021/je0002181.

(73) Breivik, K.; Wania, F.; Muir, D. C. G.; Alaee, M.; Backus, S.; Pacepavicius, G. Empirical and Modeling Evidence of the Long-Range Atmospheric Transport of Decabromodiphenyl Ether. *Environ. Sci. Technol.* **2006**, *40* (15), 4612–4618. https://doi.org/10.1021/es060730s.

(74) Besis, A.; Botsaropoulou, E.; Voutsa, D.; Samara, C. Particle-Size Distribution of Polybrominated Diphenyl Ethers (PBDEs) in the Urban Agglomeration of Thessaloniki, Northern Greece. *Atmos. Environ.* **2015**, *104*, 176–185. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2015.01.019.

(75) Luo, P.; Ni, H.-G.; Bao, L.-J.; Li, S.-M.; Zeng, E. Y. Size Distribution of Airborne Particle-Bound Polybrominated Diphenyl Ethers and Its Implications for Dry and Wet Deposition. *Environ. Sci. Technol.* **2014**, *48* (23), 13793–13799.

(76) Lyu, Y.; Xu, T.; Li, X.; Cheng, T.; Yang, X.; Sun, X.; Chen, J. Particle-Size Distribution of Polybrominated Diphenyl Ethers (PBDEs) and Its Implications for Health. *Atmos. Meas. Tech. Discuss.* **2015**, *8* (12), 12955–12992. https://doi.org/10.5194/amtd-8-12955-2015.

(77) Richman, K. E.; Butt, C. M.; Young, C. J. Size-Resolved Particle Measurements of Polybrominated Diphenyl Ethers Indoors: Implications for Sources and Human Exposure. *Environ. Toxicol. Chem.* **2018**, *37* (2), 481–490. https://doi.org/10.1002/etc.3981.

(78) Saint-Louis, R.; Pelletier, E. Sea-to-Air Flux of Contaminants via Bubbles Bursting. An Experimental Approach for Tributyltin. *Mar. Chem.* **2004**, *84* (3–4), 211–224. https://doi.org/10.1016/j.marchem.2003.08.002.

(79) Cunliffe, M.; Engel, A.; Frka, S.; Gašparović, B.; Guitart, C.; Murrell, J. C.; Salter, M.; Stolle, C.; Upstill-Goddard, R.; Wurl, O. Sea Surface Microlayers: A Unified Physicochemical and Biological Perspective of the Air-Ocean Interface. *Prog. Oceanogr.* **2013**, *109*, 104–116. https://doi.org/10.1016/j.pocean.2012.08.004.

(80) Wang, X.; Deane, G. B.; Moore, K. A.; Ryder, O. S.; Stokes, M. D.; Beall, C. M.; Collins, D. B.; Santander, M. V.; Burrows, S. M.; Sultana, C. M.; et al. The Role of Jet and Film Drops in Controlling the Mixing State of Submicron Sea Spray Aerosol Particles. *Proc. Natl. Acad. Sci.* **2017**, *114* (27), 6978–6983. https://doi.org/10.1073/pnas.1702420114.

(81) Bidleman, T.; Agosta, K.; Andersson, A.; Brorström-Lundén, E.; Haglund, P.; Hansson, K.; Laudon, H.; Newton, S.; Nygren, O.; Ripszam, M.; et al. Atmospheric Pathways of Chlorinated Pesticides and Natural Bromoanisoles in the Northern Baltic Sea and Its Catchment. *Ambio* **2015**, *44 Suppl 3*, 472–483. https://doi.org/10.1007/s13280-015-0666-4.

(82) Hultin, K. A. H.; Nilsson, E. D.; Krejci, R.; Mrtensson, E. M.; Ehn, M.; Hagström, Å.; De Leeuw, G. In Situ Laboratory Sea Spray Production during the Marine Aerosol Production 2006 Cruise on the Northeastern Atlantic Ocean. *J. Geophys. Res. Atmos.* **2010**, *115* (6), 1–19. https://doi.org/10.1029/2009JD012522.

(83) Grammatika, M.; Zimmerman, W. B. Microhydrodynamics of Flotation Processes in the Sea Surface Layer. *Dyn. Atmos. Ocean.* **2001**, *34* (2–4), 327–348. https://doi.org/10.1016/S0377-0265(01)00073-2.

(84) Hoppel, W. A.; Frick, G. M.; Larson, R. E. Effect of Nonprecipitating Clouds on the Aerosol Size Distribution in the Marine Boundary Layer. *Geophys. Res. Lett.* **1986**, *13* (2), 125–128. https://doi.org/10.1029/GL013i002p00125.

(85) O'Dowd, C. D.; Facchini, M. C.; Cavalli, F.; Ceburnis, D.; Mircea, M.; Decesari, S.; Fuzzi, S.; Yoon, Y. J.; Putaud, J.-P. Biogenically Driven Organic Contribution to Marine Aerosol. *Nature* **2004**, *431* (7009), 676–680. https://doi.org/10.1038/nature02959.

(86) Okonski, K.; Degrendele, C.; Melymuk, L.; Landlová, L.; Kukučka, P.; Vojta, Š.; Kohoutek, J.; Cupr, P.; Klánová, J. Particle Size Distribution of Halogenated Flame Retardants and Implications for Atmospheric Deposition and Transport. *Environ. Sci. Technol.* **2014**, *48* (24), 14426−14434.

(87) Cao, R.; Zhang, H.; Zhao, L.; Zhang, Y.; Geng, N.; Teng, M.; Zou, L.; Gao, Y.; Ni, Y.; Fu, Q.; et al. Hazy Weather-Induced Variation in Environmental Behavior of PCDD/Fs and PBDEs in Winter Atmosphere of A North China Megacity. *Environ. Sci. Technol.* **2018**, *52* (15), 8173–8182. https://doi.org/10.1021/acs.est.8b02148.

(88) Mandalakis, M.; Besis, A.; Stephanou, E. G. Particle-Size Distribution and Gas/Particle Partitioning of Atmospheric Polybrominated Diphenyl Ethers in Urban Areas of Greece. *Environ. Pollut.* **2009**, *157* (4), 1227–1233. https://doi.org/10.1016/j.envpol.2008.12.010.

(89) Cai, M., Ma, Y., Xie, Z., Zhong, G., Möller, A., Yang, H., Sturm, R., He, J., Ebinghaus, R., Meng, X.-Z.; Cai, M.; Ma, Y.; Xie, Z.; Zhong, G.; Möller, A.; Yang, H.; Sturm, R.; He, J.; Ebinghaus, R.; et al. Distribution and Air-Sea Exchange of Organochlorine Pesticides in the North Pacific and the Arctic. *J. Geophys. Res.* **2012**, *117* (D06311), 1–9. https://doi.org/10.1029/2011JD016910.

(90) Wania, F. Assessing the Potential of Persistent Organic Chemicals for Long-Range Transport and Accumulation in Polar Regions. *Environ. Sci. Technol.* **2003**, *37* (37), 1344–1351. https://doi.org/10.1021/es026019e.

(91) Giordano, M. R.; Kalnajs, L. E.; Avery, A.; Goetz, J. D.; Davis, S. M.; DeCarlo, P. F.; Peter, F. A Missing Source of Aerosols in Antarctica – beyond Long-Range Transport , Phytoplankton , and Photochemistry. *Atmos. Chem. Phys. Discuss.* **2016**, *17* (1), 1–31. https://doi.org/10.5194/acp-2016-606.

(92) Meyer, T.; Muir, D. C. G.; Teixeira, C.; Wang, X.; Young, T.; Wania, F. Deposition of Brominated Flame Retardants to the Devon Ice Cap, Nunavut, Canada. *Environ. Sci. Technol.* **2012**, *46* (2), 826–833. https://doi.org/10.1021/es202900u.

(93) Kim, U.-J. J.; Yen, N. T. H.; Oh, J.-E. E. Correction to Hydroxylated, Methoxylated, and Parent Polybrominated Diphenyl Ethers (PBDEs) in the Inland Environment, Korea and Potential OH- and MeO-BDE Source. *Environ. Sci. Technol.* **2014**, *48* (13), 7245–7253. https://doi.org/10.1021/es5006972.

(94) *Brominated Flame Retardants*; Eljarrat, E., Barceló, D., Eds.; The Handbook of Environmental Chemistry; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; Vol. 16. https://doi.org/10.1007/978-3-642-19269-2.

(95) Kuramochi, H.; Maeda, K.; Kawamoto, K. Physicochemical Properties of Selected Polybrominated Diphenyl Ethers and Extension of the UNIFAC Model to Brominated Aromatic Compounds. *Chemosphere* **2007**, *67* (9), 1858–1865. https://doi.org/10.1016/j.chemosphere.2006.05.076.

(96) Hale, R. C.; Alaee, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikonomou, M. G. Polybrominated Diphenyl Ether Flame Retardants in the North American Environment. *Environ. Int.* **2003**, *29* (6), 771–779. https://doi.org/10.1016/S0160-4120(03)00113-2.

(97) Lebeuf, M.; Gouteux, B.; Measures, L.; Trottier, S. Levels and Temporal Trends (1988-1999) of Polybrominated Diphenyl Ethers in Beluga Whales (Delphinapterus Leucas) from the St. Lawrence Estuary, Canada. *Environ. Sci. Technol.* **2004**, *38* (11), 2971–2977. https://doi.org/10.1021/es035187j.

(98) Burreau, S.; Zebühr, Y.; Broman, D.; Ishaq, R. Biomagnification of PBDEs and PCBs in Food Webs from the Baltic Sea and the Northern Atlantic Ocean. *Sci. Total Environ.* **2006**, *366* (2–3), 659–672. https://doi.org/10.1016/j.scitotenv.2006.02.005.

(99) McDonough, C. A.; De Silva, A. O.; Sun, C.; Cabrerizo, A.; Adelman, D.; Soltwedel, T.; Bauerfeind, E.; Muir, D. C. G.; Lohmann, R. Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram Strait. *Env. Sci Technol* **2018**, *52* (11), 6208–6216. https://doi.org/10.1021/acs.est.8b01127.

(100) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polybrominated Diphenyl Ethers (PBDEs) and Alternative Brominated Flame Retardants in Air and Seawater of the European Arctic. *Environ. Pollut.* **2011**, *159* (6), 1577–1583. https://doi.org/10.1016/j.envpol.2011.02.054.

(101) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820–1826. https://doi.org/10.1021/es103803t.

(102) Salvadó, J. A.; Sobek, A.; Carrizo, D.; Gustafsson, Ö. Observation-Based Assessment of PBDE Loads in Arctic Ocean Waters. *Environ. Sci. Technol.* **2016**, *50* (5), 2236–2245. https://doi.org/10.1021/acs.est.5b05687.

(103) Carroll, J.; Savinov, V.; Savinova, T.; Dahle, S.; Mccrea, R.; Muir, D. C. G. PCBs, PBDEs and Pesticides Released to the Arctic Ocean by the Russian Rivers Ob and Yenisei. *Environ. Sci. Technol.* **2008**, *42* (1), 69–74. https://doi.org/10.1021/es071673l.

(104) Sühring, R.; Busch, F.; Fricke, N.; Kötke, D.; Wolschke, H.; Ebinghaus, R. Science of the Total Environment Distribution of Brominated Flame Retardants and Dechloranes between Sediments and Benthic Fish — A Comparison of a Freshwater and Marine Habitat. *Sci. Total Environ.* **2016**, *542*, 578–585. https://doi.org/10.1016/j.scitotenv.2015.10.085.

(105) Van Ael, E.; Covaci, A.; Blust, R.; Bervoets, L. Persistent Organic Pollutants in the Scheldt Estuary: Environmental Distribution and Bioaccumulation. *Environ. Int.* **2012**, *48*, 17–27. https://doi.org/10.1016/j.envint.2012.06.017.

(106) Cai, M. G.; Hong, Q. Q.; Wang, Y.; Luo, X. J.; Chen, S. J.; Cai, M. H.; Qiu, C. R.; Huang, S. Y.; Mai, B. X. Distribution of Polybrominated Diphenyl Ethers and Decabromodiphenylethane in Surface Sediments from the Bering Sea, Chukchi Sea, and Canada Basin. *Deep. Res. Part II Top. Stud. Oceanogr.* **2012**, *81–84*, 95–101. https://doi.org/10.1016/j.dsr2.2011.05.006.

(107) Salvadó, J. A.; Grimalt, J. O.; López, J. F.; Durrieu De Madron, X.; Heussner, S.; Canals, M. Transformation of PBDE Mixtures during Sediment Transport and Resuspension in Marine Environments (Gulf of Lion, NW Mediterranean Sea). *Environ. Pollut.* **2012**, *168*, 87–95. https://doi.org/10.1016/j.envpol.2012.04.019.

(108) Eljarrat, E.; De La Cal, A.; Larrazabal, D.; Fabrellas, B.; Fernandez-Alba, A. R.; Borrull, F.; Marce, R. M.; Barcelo, D. Occurrence of Polybrominated Diphenylethers, Polychlorinated Dibenzo-p-Dioxins, Dibenzofurans and Biphenyls in Coastal Sediments from Spain. *Environ. Pollut.* **2005**, *136* (3), 493–501. https://doi.org/10.1016/j.envpol.2004.12.005.

(109) Verslycke, T. A.; Vethaak, A. D.; Arijs, K.; Janssen, C. R. Flame Retardants, Surfactants and Organotins in Sediment and Mysid Shrimp of the Scheldt Estuary (The Netherlands). *Environ. Pollut.* **2005**, *136* (1), 19–31. https://doi.org/10.1016/j.envpol.2004.12.008.

(110) Johnson-Restrepo, B.; Kannan, K. An Assessment of Sources and Pathways of Human Exposure to Polybrominated Diphenyl Ethers in the United States. *Chemosphere* **2009**, *76* (4), 542–548. https://doi.org/10.1016/j.chemosphere.2009.02.068.

(111) Lyche, J. L.; Rosseland, C.; Berge, G.; Polder, A. Human Health Risk Associated with Brominated Flame-Retardants (BFRs). *Environ. Int.* **2015**, *74*, 170–180. https://doi.org/http://dx.doi.org/10.1016/j.envint.2014.09.006.

(112) Hu, X.; Hu, D.; Chen, W.; Wu, B.; Lin, C. Simultaneous Determination of Methoxylated Polybrominated Diphenyl Ethers and Polybrominated Diphenyl Ethers in Water, Soil and Sediment from China by GC–MS. *J. Chromatogr. Sci.* **2015**, *53* (8), 1239–1249.

(113) Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E. Human Internal and External Exposure to PBDEs – A Review of Levels and Sources. *Int. J. Hyg. Environ. Health* **2009**, *212* (2), 109–134. https://doi.org/http://dx.doi.org/10.1016/j.ijheh.2008.04.005.

(114) Toms, L. M. L.; Hearn, L.; Kennedy, K.; Harden, F.; Bartkow, M.; Temme, C.; Mueller, J. F. Concentrations of Polybrominated Diphenyl Ethers (PBDEs) in Matched Samples of Human Milk, Dust and Indoor Air. *Environ. Int.* **2009**, *35* (6), 864–869. https://doi.org/10.1016/j.envint.2009.03.001.

(115) Guo, W., Holden, A., Smith, S. C., Gephart, R., Petreas, M., Park, J.-S. PBDE Levels in Breast Milk Are Decreasing in California. *Chemosphere* **2016**, *150*, 505–513. https://doi.org/10.1016/j.chemosphere.2015.11.032.

(116) Dimitriadou, L.; Malarvannan, G.; Covaci, A.; Iossifidou, E.; Tzafettas, J.; Zournatzi-Koiou, V.; Kalantzi, O.-I. Levels and Profiles of Brominated and Chlorinated Contaminants in Human Breast Milk from Thessaloniki, Greece. *Sci. Total Environ.* **2016**, *539*, 350–358. https://doi.org/10.1016/j.scitotenv.2015.08.137.

(117) Chen, S.-J.; Ma, Y.-J.; Wang, J.; Chen, D.; Luo, X.-J.; Mai, B.-X. Brominated Flame Retardants in Children's Toys: Concentration, Composition, and Children's Exposure and Risk Assessment. *Environ. Sci. Technol.* **2009**, *43* (11), 4200–4206. https://doi.org/10.1021/es9004834.

(118) Meerts, Ilonka A. T. M. van Zanden, J. J., Luijks, E. A. C., van Leeuwen-Bol, I., Marsh, G., Jakobsson, E., Bergman, A., Brouwer, A. Potent Competitive Interactions of Some Brominated Flame Retardants and Related Compounds with Human Transthyretin in Vitro. *Toxicol. Sci.* **2000**, *56* (1), 95–104. https://doi.org/10.1093/toxsci/56.1.95.

(119) Marchesini, G. R.; Meimaridou, A.; Haasnoot, W.; Meulenberg, E.; Albertus, F.; Mizuguchi, M.; Takeuchi, M.; Irth, H.; Murk, A. J. Biosensor Discovery of Thyroxine Transport Disrupting Chemicals. *Toxicol. Appl. Pharmacol.* **2008**, *232* (1), 150–160. https://doi.org/10.1016/j.taap.2008.06.014.

(120) Chen, D.; Hale, R. C.; Letcher, R. J. Photochemical and Microbial Transformation of Emerging Flame Retardants: Cause for Concern? *Environ. Toxicol. Chem.* **2015**, *34* (4), 687–699. https://doi.org/10.1002/etc.2858.

(121) Wang, X.; Yang, H.; Hu, X.; Zhang, X.; Zhang, Q.; Jiang, H.; Shi, W.; Yu, H. Effects of HO-/MeO-PBDEs on Androgen Receptor: In Vitro Investigation and Helix 12-Involved MD Simulation. *Environ. Sci. Technol.* **2013**, *47* (20), 11802–11809. https://doi.org/10.1021/es4029364.

2 Sampling, extraction, separation method development, and optimization

2.1 Abstract

The challenges of monitoring polybrominated diphenyl ethers (PBDE) from environmental samples include: collection of appropriate samples from outdoor environments; extraction and concentration of PBDE analytes from this bulk sample matrix; and analytical differentiation using gas chromatograph-mass spectrometry (GC-MS) between analyte congeners and to quantify their environmental concentration. This work will target the collection of PBDEs from atmospheric aerosols collected by a micro orifice uniform deposition impactor (MOUDI) setup and fish samples acquired from the Gulf of St. Lawrence and the Atlantic Ocean. Natural MeO-BDEs will also be a research focus in both sample types as their ubiquity becomes an increasing health concern. Method development is necessary to convert traditional solvent extraction techniques to accommodate new instruments (e.g. accelerated solvent extraction, ASE). Optimization of the liquid-liquid extraction will test for the most appropriate solvent ratios ideal for analyte extraction, minimal matrix effect, and considering environmental impact of solvent choice. A solvent ratio of hexane and toluene (5:1) showed the greatest signal to noise result and was implemented during the ASE extraction. Other parameters were tested with favorable PBDE extractions with 10 min exposure to 82 °C, and total 2.0 g diatomaceous earth (DE) media. The GC-MS temperature method was modified to accurately quantify PBDEs while maintaining the integrity of the analytical instrument systems to ensure numerous samples could be analyzed.

2.2 Introduction

Polybrominated diphenyl ethers (PBDEs), designated by the Stockholm Convention as persistent organic pollutants (POPs), are known to be resistant to environmental degradation[1–4]. Naturally occurring PBDE analogues, OH-BDE and MeO-BDE, produced from sponges (*Dysidea spp.*), blue mussels, and phytoplankton (*Oscillatoria spongeliae*) are additional environmental sources[5,6]. Although analysis and extraction of PBDEs from environmental samples have been ongoing since the 1970s, there is a need to revise these protocols to incorporate principles of green chemistry and better target global PBDE distribution, including naturally-occurring PBDE analogues, as new technologies become available[7]. Liquid-liquid extractions, essential to analytical methods for trace environmental PBDE levels, require suitable solvents to facilitate analyte extraction with minimal sample loss and matrix interferences associated with complex media (e.g. sediment, soil, biotic samples, etc.)[8]. The criteria for an ideal extraction solvent to remove analyte from a sample matrix requires: (i) good solvation properties (i.e. affinity for the analyte); (ii) moderate to high volatility to concentrate the analyte during the blow-down process; and (iii) minimal environmental impact. However, due to expense, limited available chemical reagents/solvents, and instrumental expertise, traditional analytical preparations (e.g. Soxhlet extraction) and reagents have remained standard practise[9].

Dichloromethane (DCM) is a conventionally used extraction solvent for extremely hydrophobic analytes in complex environmental samples. DCM has useful solvation

properties and a high vapour pressure to improve extraction efficiency. However, the DCM solvent are acutely and chronically toxic to humans and contribute significantly to stratospheric ozone depletion[10]. The need for green chemistry to develop environmentally friendly solvent alternatives can aid to mitigate costly clean up efforts while maintaining analytical efficiency. Soxhlet extraction has been commonly used to facilitate POP liquid-liquid extraction despite long extraction periods (>20 h), large solvent volume consumption, fragile glass apparatus setup, and required technical support during operation[11]. Methods of ultrasonic-assisted extraction (UAE), microwave assisted extraction (MAE), supercritical fluid extraction (SFE), and accelerated solvent extraction (ASE) represent emerging automated improvements over the Soxhlet process. UAE and MAE utilize sonic and microwave energy, respectively, to achieve analyte separation under ambient temperatures. SFE and ASE apply high temperature and pressure to increase the analyte extraction process. By improving precision and accuracy through rapid quantification, increased analysis efficiency with a wider range of sample matrices is becoming more practical and environmentally safer in industrial and research settings[9,11].

This study targeted the complex environmental matrices of atmospheric aerosols and fish liver to improve methods. Size-resolved aerosols are collected in trace quantities, thus extraction and analysis methods that maintain their integrity with minimal sample loss is essential. Weather events are commonly unpredictable, inconsistent and lead to less-than-ideal analyte sampling conditions, so ongoing maintenance and method

development is required for sample collection. For the complex fish liver matrix, analytes must be efficiently extracted from the dense fish matrix to differentiate analyte signal from experimental background. The liver is an important organ that participates in redistribution, biotransformation, accumulation, and excretion of pollutants in fish. Marine fish liver contains high levels of long chain polyunsaturated fatty acids, a prime source for PBDE accumulation, and is often used for monitoring POPs in marine environments[12–14]. This study: (i) developed sampling methods for PBDEs in size resolved aerosols; (ii) improved extraction methods for PBDEs from aerosols and fish liver samples with an emphasis on environmentally greener practises; and (iii) created a gas chromatography-mass spectrometry (GC-MS) method for the analytical evaluation of natural MeO-BDE and anthropogenic PBDE.

2.3 Materials and methods

2.3.1 Chemicals

Authentic analyte standards were purchased from Wellington Laboratories (Guelph, ON, Canada): 2’,3,4’,5-tetrabromo-2-methoxydiphenyl ether (2’-MeO-BDE-68), 2,2’,4,4’-tetrabromo-5-methoxydiphenyl ether (6-MeO-BDE-47), and a suite of 27 PBDE congeners. The BDE-MX consisted of: i) 1 µL/mL of BDE-3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, and 126; ii) 2.0 µL/mL of BDE-138, 153, 154, 156, 183, 184, 191, 196, and 197; iii) 5.0 µL/mL of BDE-206, 207, and 209. Internal standards 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (FBDE-69), 2,3,4,6-tetrabromodiphenyl ether (BDE-62), 2,3’,4,4’,5-pentabromodiphenyl ether (BDE-118), 2,2',4,5',6-pentabromodiphenyl ether

(BDE-103), and 2,2'3,3',4,5,5',6,6'-nonabromodiphenyl ether (BDE-208) were produced by AccuStandard Inc. (New Haven, CT, USA) and purchased from Chromatographic Specialties (Brockville, ON, Canada). Chromic acid, sodium perchlorate, sulphuric acid, and extraction solvents (Omnisolv DCM, toluene, acetone, and hexane) were acquired from VWR (Oakville, ON, Canada). Analytical grade N_2 gas (> 99.998% pure) was a product of Praxair Canada Inc. (Mississauga, ON, Canada). The household dust standard reference material (SRM 2585) was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Diatomaceous earth media (DE, J.T. Baker™) for the ASE setup was ordered through Thermo Fisher Scientific (Mississauga, ON, Canada). The silica gel sorbents (60-120 mesh, or 60 ECO 40-63 µm) were a product of Sigma-Aldrich (Oakville, ON, Canada).

2.3.2 Sampling methods

2.3.2.1 Atmospheric sampling

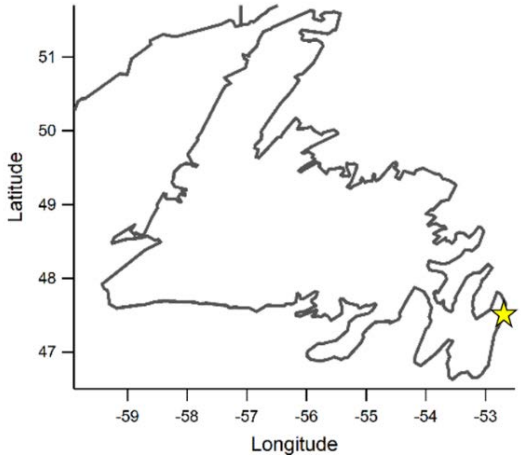

Figure 2-1. Size-resolved atmospheric collection location (47.57° N, 52.7° W, St. John's, NL, Canada) as indicated (yellow star). The two sampling locations were approximately 1 km apart and within the urban city district of St. John's, NL.

Initial atmospheric samples were collected at an urban location (Figure 2-1; 47.572° N, 52.722° W, 42 m above sea level). The secondary sampling site was at the Memorial University rooftop atmospheric sampling site (MURASS, 47.575° N, 52.734° W) at the Alexander Murray Building, a short distance from the initial sampling location. Atmospheric samples were collected by a micro orifice uniform deposit cascade impactor (MOUDI; Figure 2-2, nano-MOUDI-II 122-R, MSP Corporation, Minneapolis, MN, USA) aerosol collector. A constant air flow (30 L/min) was supplied to the MOUDI by an external vacuum pump (MDI-122-0040, MSP Corporation). The MOUDI sorted aerosols by their aerodynamic diameter from larger to progressively smaller aerosols and accumulated onto 14 substrate stages (Table 2-1). Size fractioning was accomplished by the critical trajectory of each sampling stage that would determine which aerosols would impact onto the stage versus their downward travel to the next stage below. Larger aerosols cannot bypass this critical trajectory and become impacted, whereas smaller aerosols follow the air flow to the next chamber.

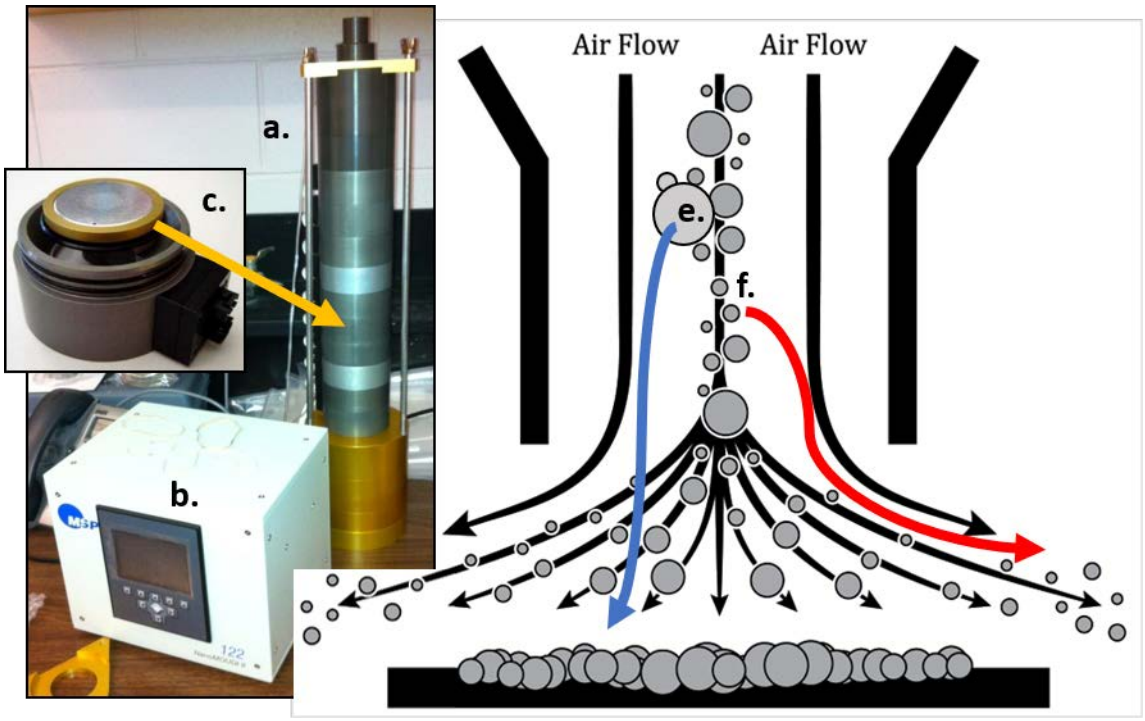

Figure 2-2. MOUDI air flow diagram: (a) stacked MOUDI substrate stages; (b) Data control box: auxiliary data collection and regulation of internal pressure between substrate collection stages; (c) substrate stage; (d) MOUDI aerodynamic critical trajectory (e) larger aerosol path results in compaction; and (f) smaller aerosol path continues to the next substrate stage chamber.

Table 2-1. Aerodynamic aerosol diameter impact ranges of each MOUDI stage.

MOUDI stage designation	Diameter cut-off (μm)
0	18
1	10
2	5.6
3	3.2
4	1.8
5	1.0
6	0.56
7	0.32
8	0.18
9	0.10
10	0.056
11	0.032
12	0.018
13	0.010

Aerosols were collected on filters punched out by hammer-driven hole punches (47 mm and 1250 mm diameters, McMaster-Carr) from Whatman glass QFF sheets (570 mm x 460 mm, Fisher Scientific) to 47 mm (stages 0 - 9) and 1250 mm (stages 10 - 13) diameters and pre-baked for at least 4 h at 500 °C. Filters were stored in Fisherbrand™ polystyrene petri dishes at 10 °C. A uniform aerosol distribution was accomplished by the inner rotation of each MOUDI substrate stage[15,16].

Substrates were secured onto a MOUDI stage with an aluminium ring clamp and then carefully positioned in their designated chamber via magnetic contacts underneath (Figure 2-1). The MOUDI chambers were stacked individually from the base nano stages, stage by stage, up to the top of the MOUDI stage stack as per instrument manufacture

design. A second set of MOUDI stages with pre-conditioned substrates were stored as a readily available backup. Care was taken to minimize contamination during substrate transfer and storage by using new nitrile gloves for each trial, pre-cleaned substrate holders and transfer equipment (e.g. tweezers, scoopula, etc.). All transfer activities were conducted in a laboratory fume hood.

Atmospheric sampling was conducted in urban St. John's, Newfoundland and Labrador (NL, Figure 2-1) with initial MOUDI sampling parameters that were based on the sampling protocol designated by Zhang *et al.* for urban Guangzhou, China[17]. A single sample was collected over 55 hours to test the applicability of these parameters. Upon removal from storage containers, aerosol substrates were carefully folded and rolled into a cylinder (collected sample side rolled inwards) and placed gently in separate new and solvent washed 15 mL glass centrifuge tubes (VWR, Oakville, ON, Canada). Each filter sample was carefully handled with new nitrile gloves between sample interactions with minimum contact to minimize cross contamination.

2.3.2.2 Fish liver samples

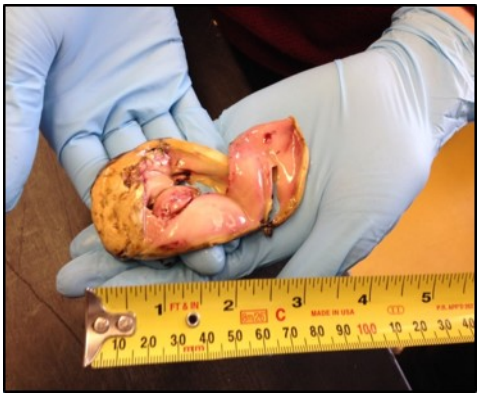

Figure 2-3. Cod liver sample (~3" length).

Atlantic cod (*Gadus Morhua*, Figure 2-3) and Greenland halibut (*Scophthalmus maximusfish*) livers were collected along the Gulf of the St. Lawrence (N = 17 cod fish, Department of Fisheries and Oceans Canada, (DFO)), Gulf of the St. Lawrence outlet (N = 5 cod fish, Marine Institute of Memorial University (MUN)), and the open Atlantic Ocean (N = 16 cod fish, N = 8 Greenland halibut, MUN Marine Institute). Fish were caught by net trawling from a ship, where livers were immediately extracted from the fish and stored in a freezer (-18 °C).

Prior to PBDE extraction, fish livers within their plastic package were brought to room temperature (~10 °C) in warm water. A ~2 g wet weight sample was removed from the bulk fish liver and uniformly homogenized for 30 seconds with a laboratory homogenizer (Tissue Tearer Homogenizer, Cole-Parmer®) before being distributed into three ~0.5 g trial runs. Fish livers are complex with a protective coating that require vigorous extraction through mechanical shearing and tearing by a homogenizer to increase sample surface area for a greater ease of PBDE analyte extraction and improved

signal. The homogenizer instrument was pre-cleaned according to manufacturing guidelines with detergent and rinsed with extraction solvent before use.

2.3.3 PBDE extraction method

During analyte extraction, both aerosol (N = 98) and fish (N = 46) samples were contained in 10 mL glass tubes. A range of 10 to 14 environmental samples were sequentially extracted with the ASE (Dionex™ 350 Heat Exchanger) setup. Each extracted ASE sample was suspended in diatomaceous earth (DE) media. These sample volumes were reduced by nitrogen gas in a multiple syringe custom setup with single use 40 mm hypodermic needles (VWR, Oakville, ON, Canada) to directly apply the nitrogen gas to each sample trial. Final clean up was performed by a solid phase extraction (SPE) with a vacuum manifold. SPE BDH™ silica gel sorbent stationary phase was used in each SPE column[18,19]. Refer to section 2.3.3.3 for more SPE extraction methodology detail.

2.3.3.1 Liquid-liquid extraction

The manual liquid-liquid extraction consisted of a 10 mL volume of extraction solvent added to each trial run. Sequential physical manipulation was performed with vortexing (20-30 s), sonication (15 min), and centrifugation (2400 rotations per minute (rpm) for 15 min) under room temperature. The extract was carefully decanted into a clean centrifuge tube. The remaining solid sample was further extracted, repeating the process for a total of 3 extractions. These extracts were combined, sealed, and stored at -10 °C. The solvent volume was reduced to ~0.5 mL under a gentle stream of nitrogen gas using a custom setup. Each sample was reduced under a 10 mL syringe with a single use

needle that hovered (~1 mm) above the sample surface for direct nitrogen gas application. A new needle was used for each sample. The final analyte volume was transferred to a 1.5 mL GC vial and stored at -10 °C.

2.3.3.2 Accelerated solvent extraction (ASE)

The manual sample extraction process was improved with an automated analytical ASE instrument. ASE cells consisted of a screw cap at both ends of the cell, where a filter was positioned at the bottom. Preparation of ASE cells and glass cylinder collectors with their caps consisted of an initial soap wash and then a solvent rinse. New filters and septa for the glass cylinder collectors were solvent rinsed. DE was the bulk media for holding the sample in each ASE cell[9]. DE media was pre-baked for 4 hours (500 °C) and acclimatized to < 100 °C before use. Method extraction was based on a *Ghosh et al.*[20,21] protocol. The following parameters were consistent in each sample trial: 100 °C, 1500 psi, 100 second nitrogen gas purge and 5 min heat-up time with 3 extractions per sample in static mode (5 min)[21]. Each ASE cell produced a total extracted volume of 100 to 150 mL that was blown down with N_2 gas to a ~500 µL volume.

2.3.3.3 Sample clean-up

Clean-up of the extracted sample was accomplished with SPE. The aim of the clean-up was to maximize matrix retention and minimize analyte retention within the SPE column, while minimizing solvent and time usage by customizing the cleanup and fractionation processes in a single step. Manually packed commercial inert polar silica gel made up the SPE stationary phase[22]. Silica gel and glass wool were pre-baked for ~4 hours

at 500 °C prior to use. SPE columns and manifold were washed with soap and rinsed with deionized water and then extraction solvent prior to use. The SPE column was initially packed with glass wool at the base to allow effluent to pass while securing the stationary phase. A second layer of sodium perchlorate (~0.5 g) was uniformly applied as a drying agent. The bulk material of the stationary phase primarily consisted of ~20 g silica gel. Before sample clean-up, an initial extraction solvent of 10 mL was used to activate the column. After the sample (~1 mL) had been added to the activated column, three additional solvent rinses using equivalent solvent volumes to that of the stationary phase volume was used and collected to adequately remove analyte residue from the SPE column[23]. The resulting diluted extracted samples were collected in numerous centrifuge tubes and then combined into one volume, followed by N_2 volume reduction (as described in section 2.3.3.1). This dilute sample extract may fill numerous centrifuge tubes depending on how complex the sample matrix was.

2.3.4 Quality assurance/quality control

All PBDE quantifications were accomplished by internal standard calibration standard using BDE-118. Instrumental GC-MS variability was accounted for by triplicate GC injection. After sample clean-up and blow-down procedure steps, 1.5 µL volume of the internal standard BDE-118 (2 µg/mL solution) was added to each sample aliquot (~250 µL) prior to GC-MS injection. Method detection limits were calculated for the MOUDI setup with pre-baked Whatman QFF field blanks exposed to the ambient environment for a few seconds during atmospheric sampling. Literature NIST 2585 SRM contained certified

concentrations of all PBDE congeners to accurately quantify sample PBDE concentrations as described in Chapter 3**.**

2.3.5 GC-ECNI-MS method

PBDE analysis was performed with an Agilent (Palo Alto, CA, USA) GC (6890) coupled to a MS (5875C) in electron capture negative ionization (ECNI) mode at 70 eV[19,22] using methane as the reagent gas. The MS was calibrated using a perfluoro-5,8-dimethyl-3,6,9-trioxidodecane (PFDTD) standard operated under autotune parameters. A new temperature program was developed to resolve a mixed standard of 27 PBDEs (BDE-MX) along with additional standards: 2'-MeO-BDE-68, 6-MeO-BDE-47, FBDE-69, BDE-62, BDE-118, BDE-103, and BDE-208 (Wellington Laboratories, Guelph, ON). Samples were injected via an Agilent autosampler (7683) with 3 needle pre-washes of acetone, hexane and analyte respectively, before drawing a final volume of 1 µL into the injection port under splitless injection mode (320 °C injection temperature, 4.0 min splitless-time)[24]. Injected analytes were separated with an Agilent DB-5HT capillary column. The injection port was held at 260 °C and the MS transfer line was maintained at 280 °C. The oven temperature program consisted of an initial 5 min hold at 100 °C followed by a temperature ramp of 25 °C/min to 250 °C, a second temperature ramp of 5 °C/min to 265 °C, and then concluded with a 25 °C/min ramp to 325 °C and a temperature hold of 4.75 min for a total run time of 26.4 min. Helium carrier gas flow rate was constant at 1.5 mL/min. PBDEs analyzed using GC-ECNI-MS were quantified using bromide anions (79 and 81 *m/z*) and confirmed using 161 and 247 *m/z*[25–27] by means of selected ion monitoring (SIM) mode.

Assessments of external standard, internal standard and standard addition calibrations will be described in Chapter 3.

2.4 Results and discussion

2.4.1 Aerosol sampling optimization

Figure 2-4. Memorial university rooftop atmospheric sampling site (MURASS) setup: (A) micro orifice uniform deposit cascade impactor (MOUDI) sampler, (B) high volume sampler, (C) medium volume sampler.

The majority of PBDE studies via MOUDI collection have occurred in urban settings. Zhang *et al.*[17] conducted atmospheric collections in Guangzhou, China and were used as the basis for this study's initial experimental protocol. Anthropogenic PBDE levels in our study at St. John's, Newfoundland (2016 population ~108,860[28]) was expected to be lower in comparison to the more densely populated Guangzhou, China (2016 population > 13,000,000 population[29]). Thus, initial collected samples in St. John's were

collected for ~4 times longer than the Guangzhou study (12 hours: 543-949 pg/m^3 total PBDE in particulate and gaseous phases)[17]. However, our MOUDI setup collected a combined total aerosols of < 20 mg. This total mass was measured as a difference of the initial filter substrate mass from the mass of the filter after sample collection. All PBDEs were below the limits of detection for each MOUDI stage. An upper limit of total PBDE content of < 54 pg/m^3 was estimated. This indicated that a longer sampling time was required to obtain quantifiable levels of PBDEs.

To improve on sample collection, the MOUDI setup was relocated as part of the MURASS collection site close to the original site. This location was approximately 23 m above ground level (58 m above sea level) at a site that allowed long-term collection of aerosols in St. John's. A revised sampling time of ~1 month was used to ensure sufficient aerosols were collected for quantitative analysis. The MOUDI setup and vacuum pump had custom-built protection from wind and weather exposure. A stainless-steel casing (Figure 2-4) elevated on a stand and anchored by heavy concrete supports was constructed for the MOUDI sampling plate stack and its electrical box. A 1 m tall total suspended particulate inlet (URG Corp., Chapel Hill, NC, USA) at the top of the MOUDI setup was installed to allow for surrounding air to be drawn into the weatherproof box without sampling obstruction. Connections from the vacuum pump to the MOUDI and the aerosol inlet were sealed with duct seal putty to minimize interior moisture. A weather-stripped secured door allowed for the removal and maintenance of the MOUDI. Pressure readings along the MOUDI sampling plate stack were recorded at the beginning and

ending of each sampling period with weekly observations to ensure stage pressures were operating according to manufacturer guidelines. The vacuum pump electronics were protected with a custom-built weatherproof box and suspended on a custom-built wheeled transport system to facilitate easy movement of the pump (68 kg)[15]. The vacuum pump exhaust line extended 20 m from the MOUDI inlet to prevent contamination. Pump maintenance consisted of changing the filter (BUSCH™ filter oil) and vacuum pump oil (BUSCH™ vacuum pump, R-580, R-530S) every sampling period (~30 days). The high-efficiency particulate air (HEPA) filter at the exhaust of the vacuum pump was changed every approximately 90 sampling days. All replacement filters and oil were as described by MSP Corp. manufacturing recommendation.

Sampling time was recorded to determine PBDE concentration as a product of the MOUDI air flow. A total of seven MOUDI sample sets were collected from July 2015 and October 2016. PBDEs and MeO-BDEs could be detected in these samples indicating the method was suitable. Results are described in Chapter 4.

2.4.2 Analyte extraction optimization

2.4.2.1 Analyte extraction solvent selection

Table 2-2. Properties of organic solvents for PBDE extraction.

Solvent (OmniSolv®)	Vapour pressure (hPa) at 293 K	Intermolecular forces	Environmental impact
Acetone	233	Fixed dipole	VOC
Dichloromethane	475	H-bond donor (very weak)	Stratospheric ozone depletion
Ethyl acetate	97	Fixed dipole	VOC
Hexane	176	Dispersion	VOC
Toluene	29	Induced dipole (∏-∏)	VOC

*VOC = volatile organic carbon

Standard extraction methods use DCM as an extraction solvent for aromatic POP analytes. As the only common solvent that is a monopolar hydrogen bond donor, DCM is ideal for solvation of compounds that are monopolar hydrogen bond acceptors (e.g. polycyclic aromatic hydrocarbons). However, multiple halogens on the aromatic rings reduce the hydrogen bond acceptor character of the aromatic rings[4]. Thus, use of DCM likely does not provide the same benefits for extraction of PBDEs compared to non-halogenated aromatic compounds and may not be an ideal choice for PBDE analytes. Volatilized DCM molecules become exposed to UV radiation in the stratosphere that dissociate chlorine radicals and promotes ozone depletion through these radical's immediate reaction with O_3[10]. Whereas other solvents were able to form ground-level ozone from initial solvent interactions with hydroxyl radicals that would catalyze nitrogen

oxides towards O_3 production[30]. Use of other solvents to extract PBDEs could be an improvement in multiple ways. Hexane, toluene, and acetone are greener solvent extraction alternatives that do not deplete the stratospheric ozone layer and could provide equivalent extraction efficiency[10]. Along with solvation properties, solvent volatilities were considered to create an efficient analyte extraction since a solvent blow-down step was required. An ideal solvent ratio mixture was determined from various trial combinations of hexane, acetone, and toluene (Table 2-2) to discover the most appropriate solvent for extraction. Hexane was the primary solvent in most solvent ratios and extraction procedures because of its non-polarity (solely dispersion forces) and its high volatility at room temperature[31]. Acetone and ethyl acetate are more volatile than hexane but have greater inter-molecular forces (i.e. fixed dipole). Toluene has a ring structure that could form ∏-∏ interactions to select for PBDEs analytes during extraction. Although hexane, acetone, ethyl acetate, and toluene are considered volatile organic compounds and can contribute to the formation of ground-level ozone, the additional impact of the solvent use for these extractions is expected to be small.

Liquid-liquid extractions were performed on SRM 2585 household dust and locally caught fish samples. Fish (1.00 – 0.50 g) and dust sample masses were recorded before extraction. Dust samples were used as a proxy for size-resolved atmospheric aerosol samples since these real aerosol samples were difficult to collect, have small sample sizes, and that PBDEs were commonly detected in dust[32]. Generally, the aerosol matrix was expected to be similarly complex. Dust samples were weighed at ~150 mg into a 15 mL

centrifuge tube. Initial sample preparation involved the addition of extraction solvent (10 mL) to each centrifuge tube. Vortex application for 20-30 s, followed by sonification for 15 min and centrifuge for 15 min at 2400 rpm was performed. Solvent combinations tested (Table 2-3) included hexane (H), toluene (T), acetone (A), and ethyl acetate (EA).

Table 2-3. Extraction solvent combinations tested and observed PBDE signal to noise ratio (S/N) from GC-MS analysis of cod fish liver.

Solvent ingredients	Solvent volume ratio	Solvent volume	PBDE S/N		
			BDE-28	BDE-47	BDE-154
Hexane : Toluene	1 : 1	30 mL	3	11	38
Hexane : Toluene	1 : 1	10 mL	4	15	54
Hexane : Toluene	9 : 1	30 mL	4	18	54
Hexane : Toluene : Acetone	2 : 1 : 1	30 mL	4	16	49
Hexane : Ethyl Acetate	1 : 1	30 mL	2	9	31

Stapleton *et al.*[23] suggested that varying solvent polarity with a mixture of available extraction solvents could improve analyte separation and signal to noise ratio (S/N). Initial testing showed improved S/N with trials H:T:A and H:T. Fish sample matrices were more complex than SRM house dust and were shown to have a lower S/N with the H:T:A trial. This may be attributed to the nature of the acetone solvent extracting more molecularly polar fish material. Therefore, the 30 mL H:T (9:1) trial was chosen as the most effective extraction solvent according to its GC-electron capture negative ionization (ECNI)-MS chromatograph with the highest S/N among solvent trails. Ghosh *et al.*[20] also showed an increased PBDE S/N when hexane was the larger component within the extraction solvent. Although a H:T extraction solvent may volatilize slower than a DCM

extraction due to toluene's low vapor pressure, this 9:1 (H:T) ratio makes its associated N_2 solvent blow step comparable to DCM in terms of time.

2.4.2.2 Fish matrix cleanup

After applying the SPE cleanup method described above (Section 2.3.3.3), the analysis of fish extracts showed PBDE peak shifting, indiscriminate peak resolution, and large baseline discrepancies with increasing retention time that meant matrix effect was still a significant factor. Sample matrix effects may have also contributed to inflated S/N and a general upward baseline tailing at the end of the chromatograph. Further examination of analyte separation from the sample fish matrix was required.

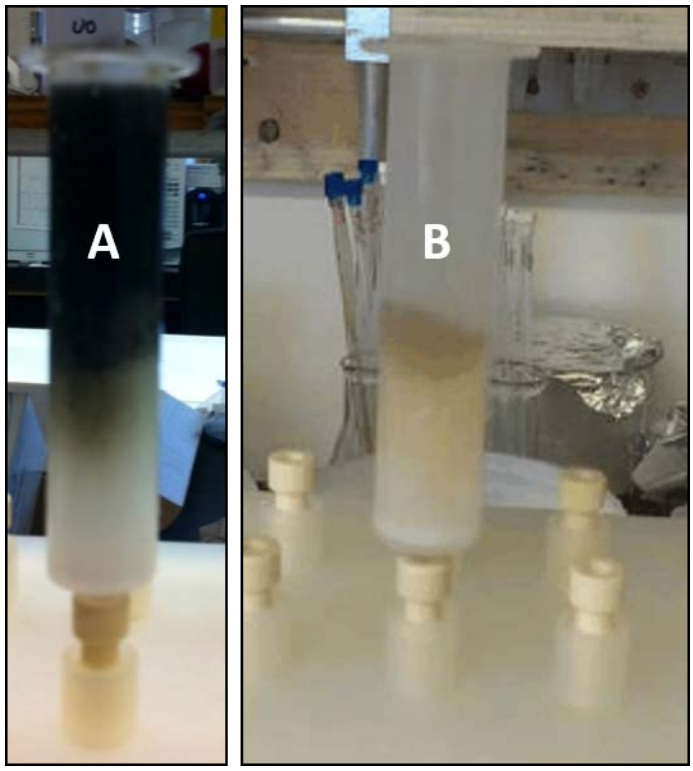

Figure 2-5. SPE fish extraction: (A) preliminary 10 mL SPE column trial, lipid separation (upper dark region) in acidified silica gel stationary phase; (B) improved analyte separation with an increased stationary phase volume.

The SPE cleanup process was adequate for aerosol samples; however, fish livers required a greater separation quality in the SPE stationary phase media. A sulfuric acid-treated silica gel (~40 % w/w) treatment was created to break down lipids associated with fish liver extract. In Figure 2-5, lipid breakdown could be visually seen by a browning colour within the stationary phase. A 300 % increase (~20 g) from the initial stationary phase quantity (i.e. acidified silica gel) and the replacement of 10 mL SPE columns that was originally used with a larger volume 30 mL SPE column ensured a greater exposure of this stationary phase to the sample matrix during analyte extraction. Solvent rinsing was halted before this browning layer approached the column base to prevent fish lipids from being eluted from the SPE stationary phase. If necessary, additional new SPE columns were used until the sample solvent rinses could be completed without the brown layer reaching the bottom of the SPE stationary phase. Column length and depth determine time of travel for the bulk sample to go through and actively associate with the stationary phase, allowing for a majority of analyte to be separated from the matrix.

2.4.3 Accelerated solvent extraction (ASE)

2.4.3.1 Method optimization

Method development was required to determine suitable ASE parameters for efficient analyte extraction from fish liver and atmospheric aerosols. One fish sample was consistently used throughout this method optimization with the assumption that results would translate to aerosol samples since the atmospheric matrix was less complex. The physical media (DE and solvent) and the analysis parameters (temperature and time) were

evaluated (Table 2-4) to determine the ideal setting for PBDE extraction. Due to the physical restrictions of the automated system and the volume of each individual ASE cell, the solvent composition had to be adjusted from the previously determined hexane:toluene ratio (9:1) to the revised ASE solvent ratio of 5:1.

2.4.3.2 Extraction media

Table 2-4. Accelerated solvent extraction (ASE) sample cell extraction media analysis.

Trial	1st layer	2nd layer	3rd layer	Solvent	Ratio	BDE-118 (S/N)
Blank	DE 1.9 g	N/A	N/A	Hexane:Toluene	5:1	85
1	DE 1.5 g	Fish liver, 0.5 g	DE 0.5 g	Hexane:Toluene: Acetone	2:1:1	252
2	Silica 2 g, DE 1 g	Fish liver, 0.5 g	DE 0.1 g	Hexane:Toluene	5:1	150
3	DE 1.5 g	Fish liver, 0.5 g	DE 0.5 g	Hexane:Toluene	5:1	538

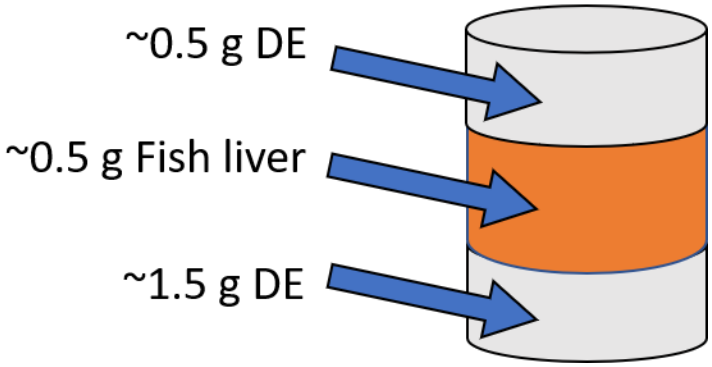

Figure 2-6. Accelerated solvent extraction (ASE) cell trial #3 schematic.

Variations of the extraction solvent ratios with varying DE volumes and weights (Table 2-4) were based on previous literature[20,33]. Figure 2-6 illustrates an example of this media distribution within the ASE cell. According to the resultant S/N results, trial 3 gave

the greatest analyte resolution and S/N. The hexane-toluene solvent ratio in trial 3 was comparable to the previous successful solvent extraction ratio (9:1) in the SPE setup. The silica gel in Table 2-4, trail 2 showed no effect in chromatographic separation, therefore was not included as part of the final method.

2.4.3.3 Temperature program

As the most successful trial from the previous ASE analysis, trial 3 was then used for the next method optimization step (Table 2-5) that tested temperature and sample duration. The blank trial run was performed using no fish sample. Fish extractions from trial A seemed to have responded at an optimum under moderate temperature and exposure. A temperature (100 °C) and exposure time (10 min) may be high enough to degrade liver lipids to liberate the analyte while performing at a low enough temperature to preserve the PBDEs themselves.

Table 2-5. ASE sample cell temperature program analysis.

Trial	Temperature	Duration
Blank	100 °C	10 min
A	82 °C	10 min
B	120 °C	10 min
C	100 °C	5 min
D	100 °C	15 min

2.4.4 Analytical method

2.4.4.1 MS method

Available MS ionizations for PBDE analysis in GC is ECNI and electron ionization mode (EI). Analyte ionization through EI will create many fragments from the collision of electrons and analyte. The ECNI mode is common for analysis of halogen-containing

compounds due to their characteristic ability to accept a lower-energy electron from a charged ionization gas (e.g. methane). In the case of PBDE analytes, ECNI leads to extensive fragmentation and formation of primarily bromide anions (79 and 81 *m/z*). ECNI was chosen for experimentation due to its great selectivity to halogenated analytes that consequently leads to a lower noise background and higher S/N. Quantification in ECNI is achieved using the bromide anion, with additional confirmation provided by characteristic fragments at 161 *m/z* $[HBr_2]^-$, and 323/327 *m/z* $[M\text{-}H\text{-}2Br]^-$ [23]. Improved PBDE selectivity and decreased sample run duration can be accomplished with the application of atmospheric pressure chemical ionization (APCI) and photoionization (APPI) to GC-ECNI-MS[8].

2.4.4.2 Development of GC separation method

An ideal chromatogram may be attained by a GC temperature program that produces resolved narrow peaks that can be differentiated between standards and other brominated compounds. The Environmental Protection Agency (EPA) have created a protocol for PBDE analysis known as method 1614 that is the gold standard[1]. However, Wellington Laboratories Inc. had created a temperature program for the separation of their standard BDE-MX that consisted of one temperature ramp. This was accomplished using GC-EI-MS in tandem with high resolution mass spectrometry (HSMS) and did not include several of our PBDE target analytes. Other PBDE studies have streamlined their GC temperature programs to one or two temperature ramps given their tandem setup with HSMS or inductively coupled plasma (ICP)-MS[2–6]. PBDE standards in this study were

separated with a 15 m DB-5HT (0.25 mm id, 0.1 µm film thickness) GC column that utilized a temperature program developed to optimize separation as discussed in section 2.3.5. This GC temperature program was similar to the EPA methodology in that both had three temperature ramps that approached comparable temperature parameters. The method in this study used GC-MS analysis conducted under ECNI mode for better selectivity with a temperature program that consisted of an initial step of 90 °C for 2 min. Peak resolution became difficult around the 10.40 to 12.20 min range where numerous peaks co-eluted, specifically the separation of the MeO-BDE standards from the other anthropogenic PBDE standards. The analytes were identified by their characteristic retention times and MS fragmentation based on the confirmation ions of 161 and 323/327 *m/z* .

2.4.4.3 PBDE-specific GC maintenance

Efforts to preserve the general structure of this sensitive PBDE analyte require constant maintenance and replacement GC components. Unfortunately, the high temperatures required for efficient GC separation were also conditions that readily degrade the PBDE analyte. Larger brominated PBDE (e.g. BDE 209) were more susceptible to temperature breakdown than smaller structures. The resultant residue, combined with matrix deposits, accumulated along the interior of the instrument and would consequently decrease signal sensitivity and the lifetime operation of instrumental components. A short-term solution was to maintain the GC column in the GC at 300 °C for ~4-24 hours to remove contaminants. The GC injection port was another source of signal loss. The injection temperature necessary to completely volatilize analytes was decreased

to 320 °C with a 4.0 min splitless time in order to preserve molecular structure integrity[34]. Interior GC components that are exposed to the sample were consistently replaced. GC components that were regularly replaced were the Agilent front inlet septa and inlet liner (replaced per ~50-100 injections), gold seal (replaced per ~500-1000 injections), and GC column (replaced per ~100-500 injections and 30 cm cut from the injector end per ~100 injections, depending on matrix). An acid wash of the inlet liner allowed this component to be reused. Sonication with chromic acid for ~5 min was conducted on dirty inlet liners followed by distilled deionized water (~5 min) and then a final solvent (hexane:toluene, 9:1) rinse. The frequency of replacement GC components was determined by sample matrices, more complex environmental matrices increased the rate of replacement parts. The GC column was replaced every ~100 fish sample injections or every ~500 aerosol sample injections. Sample types were injected in series, one after the other, to maximize the GC column's life span with aerosol sample sets being injected before fish sample sets.

With the intention to increase GC column longevity and improve analyte signal, the utilization of a shorter length 15 m GC column has become an accepted practise for halide POPs[23]. This allowed for a greater probability of PBDE components to be separated and analyzed before significant degradation, and to decrease residue build up. The injector end of the GC column was routinely trimmed (~30 cm) if either a consistent linear chromatographic baseline could not be maintained or ~100 samples had been injected. After column trimming, the GC column was baked for ~12 hours and an autotune program with the perfluoro-5,8-dimethyl-3,6,9-trioxidodecane (PFDTD) standard run before the

PBDE analysis continued. Whenever an autotune showed low MS efficiency (i.e. decreased vacuum pump speed, depleted He gas levels, and minimal filament current), the ECNI source was cleaned and the filament checked if replacement was required. About ~20 % of injections were QA/QC (e.g. solvent blanks, PBDE standards) to determine GC column integrity, analyte concentrations, peak width broadening and instrumental drift. This practice was imperative for long sequence sample runs (~days).

2.5 Conclusions

Aerosols collected from the MOUDI setup and fish liver samples were analyzed for PBDE concentrations. Due to the relatively lower aerosol and PBDE concentrations associated with less populated urban cities (i.e. NL) compared to China, sample collection times were increased to one month and atmospheric sampler sites moved to a permanent sampling site. During analysis the intention to quantifiably extract the PBDE analyte from its sample matrix was essential to minimize matrix effects while optimizing an analytical method that was both precise and environmentally safe. A hexane:toluene (9:1) solvent extraction was selected to be the most efficient solvent to remove the PBDE analyte from the sample matrices. It was speculated that the toluene solvent induces ∏-∏ interactions with the PBDE ring structure to remove the analyte where the greater hexane content rapidly volatilizes to isolate the PBDE for GC-MS analysis. This was a great improvement from the environmentally detrimental DCM solvent. The parameters used from the manual liquid-liquid extraction were modified by the automated ASE instrument which also determined that hexane and toluene were adequate for analyte separation with this

setup. A clean up SPE setup was used and improved upon with a greater use (300% more) of the acidified silica stationary phase. Since fish liver was a complex matrix, method development for this sample became a proxy for the less complicated aerosol samples collected from the MOUDI setup. PBDE analysis was performed by GC-MS. Method development to obtain the most ideal GC temperature separation program was focused on acquiring the greatest signal to noise by maintaining the integrity of this temperature sensitive analyte. When this PBDE analyte did breakdown during analysis, the GC-MS was monitored, and components were replaced or modified (GC column trimming) to continue analyzing numerous samples.

2.6 References

(1) Secretariat of the Stockholm Convention on Persistent Organic Pollutants United Nations Environment Programme (UNEP) Chemicals International Environment House. *Ridding the World of POPs: A Guide to the Stockholm Convention*; United Nations Environment Programme: Châtelaine, Geneva, Switzerland, 2005.

(2) Ezechiáš, M.; Covino, S.; Cajthaml, T. Ecotoxicity and Biodegradability of New Brominated Flame Retardants: A Review. *Ecotoxicol. Environ. Saf.* **2014**, *110*, 153–167. https://doi.org/10.1016/j.ecoenv.2014.08.030.

(3) Johnsen, A. R.; Wick, L. Y.; Harms, H. Principles of Microbial PAH-Degradation in Soil. *Environ. Pollut.* **2005**, *133* (1), 71–84. https://doi.org/10.1016/j.envpol.2004.04.015.

(4) Kov, A. Halogen Acceptors in Hydrogen Bonding. **2006**, *250*, 710–727. https://doi.org/10.1016/j.ccr.2005.04.031.

(5) Wiseman, S. B.; Wan, Y.; Chang, H.; Zhang, X.; Hecker, M.; Jones, P. D.; Giesy, J. P. Polybrominated Diphenyl Ethers and Their Hydroxylated/Methoxylated Analogs: Environmental Sources, Metabolic Relationships, and Relative Toxicities. *6th Int. Conf. Mar. Pollut. Ecotoxicol.* **2011**, *63* (5–12), 179–188. https://doi.org/http://dx.doi.org/10.1016/j.marpolbul.2011.02.008.

(6) Unson, M. D.; Holland, N. D.; Faulkner, D. J. A Brominated Secondary Metabolite Synthesized by the Cyanobacterial Symbiont of a Marine Sponge and Accumulation of the Crystalline Metabolite in the Sponge Tissue. *Mar. Biol.* **1994**, *119* (1), 1–11. https://doi.org/10.1007/BF00350100.

(7) Vonderheide, A. P.; Mueller, K. E.; Meija, J.; Welsh, G. L. Polybrominated Diphenyl Ethers: Causes for Concern and Knowledge Gaps Regarding Environmental Distribution, Fate and Toxicity. *Sci. Total Environ.* **2008**, *400* (1), 425–436.

(8) Papachlimitzou, A.; Barber, J. L.; Losada, S.; Bersuder, P.; Law, R. J. A Review of the Analysis of Novel Brominated Flame Retardants. *J. Chromatogr. A* **2012**, *1219*, 15–28. https://doi.org/http://dx.doi.org/10.1016/j.chroma.2011.11.029.

(9) Subedi, B.; Aguilar, L.; Robinson, E. M.; Hageman, K. J.; Björklund, E.; Sheesley, R. J.; Usenko, S. Selective Pressurized Liquid Extraction as a Sample-Preparation Technique for Persistent Organic Pollutants and Contaminants of Emerging Concern. *TrAC Trends Anal. Chem.* **2015**, *68*, 119–132. https://doi.org/10.1016/j.trac.2015.02.011.

(10) Hossaini, R.; Chipperfield, M. P.; Montzka, S. A.; Leeson, A. A.; Dhomse, S. S.; Pyle, J. A. The Increasing Threat to Stratospheric Ozone from Dichloromethane. *Nat. Commun.* **2017**, *8*, 1–9. https://doi.org/10.1038/ncomms15962.

(11) Wang, P.; Zhang, Q.; Wang, Y.; Wang, T.; Li, X.; Ding, L.; Jiang, G. Evaluation of Soxhlet Extraction, Accelerated Solvent Extraction and Microwave-Assisted Extraction for the Determination of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in Soil and Fish Samples. *Anal. Chim. Acta* **2010**, *663* (1), 43–48. https://doi.org/10.1016/j.aca.2010.01.035.

(12) Laboratories, I. F. The Effect of Nutritional Status of Icelandic Cod (Gadus. *North* **1999**, *16*, 111–129.

(13) Shinn, C.; Dauba, F.; Grenouillet, G.; Guenard, G.; Lek, S. Temporal Variation of Heavy Metal Contamination in Fish of the River Lot in Southern France. *Ecotoxicol. Environ. Saf.* **2009**, *72* (7), 1957–1965. https://doi.org/10.1016/J.ECOENV.2009.06.007.

(14) Guil-Guerrero, J. L.; Venegas-Venegas, E.; Rincón-Cervera, M. Á.; Suárez, M. D. Fatty Acid Profiles of Livers from Selected Marine Fish Species. *J. Food Compos. Anal.* **2011**, *24* (2), 217–222. https://doi.org/10.1016/J.JFCA.2010.07.011.

(15) Corporation, M. Impactor Selection Guide – Aerosol Research, 2017.

(16) Marple, V. A.; Rubow, K. L.; Behm, S. M. A Microorifice Uniform Deposit Impactor (Moudi): Description, Calibration, and Use. *Aerosol Sci. Technol.* **1991**, *14* (4), 434–436. https://doi.org/10.1080/02786829108959504.

(17) Zhang, B.-Z.; Zhang, K.; Li, S.-M.; Wong, C. S.; Zeng, E. Y. Size-Dependent Dry Deposition of Airborne Polybrominated Diphenyl Ethers in Urban Guangzhou, China. *Environ. Sci. Technol.* **2012**, *46* (13), 7207–7214.

(18) Barón, E.; Eljarrat, E.; Barceló, D. Gas Chromatography/Tandem Mass Spectrometry Method for the Simultaneous Analysis of 19 Brominated Compounds in Environmental and Biological Samples. *Anal. Bioanal. Chem.* **2014**, *406* (29), 7667–7676. https://doi.org/10.1007/s00216-014-8196-7.

(19) Aznar-Alemany, Ò.; Trabalón, L.; Jacobs, S.; Barbosa, V. L.; Tejedor, M. F.; Granby, K.; Kwadijk, C.; Cunha, S. C.; Ferrari, F.; Vandermeersch, G.; et al. Occurrence of Halogenated Flame Retardants in Commercial Seafood Species Available in European Markets. *Food Chem. Toxicol.* **2017**, *104*, 35–47. https://doi.org/10.1016/j.fct.2016.12.034.

(20) Ghosh, R.; Hageman, K. J.; Bjorklund, E. Selective Pressurized Liquid Extraction of Three Classes of Halogenated Contaminants in Fish. *J. Chromatogr. A* **2011**, *1218* (41), 7242–7247. https://doi.org/10.1016/j.chroma.2011.08.052.

(21) Losada, S.; Santos, F. J.; Galceran, M. T. Selective Pressurized Liquid Extraction of Polybrominated Diphenyl Ethers in Fish. *Talanta* **2009**, *80* (2), 839–845. https://doi.org/10.1016/j.talanta.2009.08.002.

(22) Kalachova, K.; Cajka, T.; Sandy, C.; Hajslova, J.; Pulkrabova, J. High Throughput Sample Preparation in Combination with Gas Chromatography Coupled to Triple Quadrupole Tandem Mass Spectrometry (GC-MS/MS): A Smart Procedure for (Ultra)Trace Analysis of Brominated Flame Retardants in Fish. *Talanta* **2013**, *105* (August 2004), 109–116. https://doi.org/10.1016/j.jmbbm.2014.11.004.

(23) Stapleton, H. M. Instrumental Methods and Challenges in Quantifying Polybrominated Diphenyl Ethers in Environmental Extracts: A Review. *Anal. Bioanal. Chem.* **2006**, *386* (4), 807–817.

(24) Richman, K. E.; Butt, C. M.; Young, C. J. Supplemental: Size-Resolved Particle Measurements of Polybrominated Diphenyl Ethers Indoors: Implications for Sources and Human Exposure. *Environ. Toxicol. Chem.* **2018**, *37* (2), 481–490. https://doi.org/10.1002/etc.3981.

(25) Losada, S.; Santos, F. J.; Covaci, A.; Galceran, M. T. Gas Chromatography–Ion Trap Tandem Mass Spectrometry Method for the Analysis of Methoxylated Polybrominated Diphenyl Ethers in Fish. *J. Chromatogr. A* **2010**, *1217* (32), 5253–5260. https://doi.org/http://dx.doi.org/10.1016/j.chroma.2010.06.023.

(26) Vetter, W. A GC/ECNI-MS Method for the Identification of Lipophilic Anthropogenic and Natural Brominated Compounds in Marine Samples. *Anal. Chem.* **2001**, *73* (20), 4951–4957. https://doi.org/10.1021/ac015506u.

(27) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-Retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254. https://doi.org/10.1021/es060630m.

(28) Agency, N. & L. S. *Population by Census Subdivsion (CSD) Newfoundland and Labrador 2016 Census*; 2016. https://doi.org/98-402-X2016001.

(29) Guangzhou Population 2017 https://countrydigest.org/guangzhou-population/#Guangzhou_population_by_year.

(30) Lelieveld, J.; Dentener, F. J. What Controls Tropospheric Ozone? *J. Geophys. Res. Atmos.* **2000**, *105* (D3), 3531–3551. https://doi.org/10.1029/1999JD901011.

(31) Bichon, E.; Guiffard, I.; Vénisseau, A.; Lesquin, E.; Vaccher, V.; Marchand, P.; Le Bizec, B. Simultaneous Analysis of Historical, Emerging and Novel Brominated Flame Retardants in Food and Feed Using a Common Extraction and Purification Method. *Chemosphere* **2018**, *205*, 31–40. https://doi.org/10.1016/j.chemosphere.2018.04.070.

(32) Bjorklund, J. A.; Thuresson, K.; Cousins, A. P.; Sellstrom, U.; Emenius, G.; De Wit, C. A. Indoor Air Is a Significant Source of Tri-Decabrominated Diphenyl Ethers to Outdoor Air via Ventilation Systems. *Environ. Sci. Technol.* **2012**, *46* (11), 5876–5884. https://doi.org/10.1021/es204122v.

(33) Hu, X.; Hu, D.; Chen, W.; Wu, B.; Lin, C. Simultaneous Determination of Methoxylated Polybrominated Diphenyl Ethers and Polybrominated Diphenyl Ethers in Water, Soil and Sediment from China by GC–MS. *J. Chromatogr. Sci.* **2015**, *53* (8), 1239–1249.

(34) Björklund, J.; Tollbäck, P.; Hiärne, C.; Dyremark, E.; Östman, C. Influence of the Injection Technique and the Column System on Gas Chromatographic Determination of Polybrominated Diphenyl Ethers. *J. Chromatogr. A* **2004**, *1041* (1–2), 201–210. https://doi.org/10.1016/j.chroma.2004.04.025.

3 Development of new calibration methods for analysis of polybrominated diphenyl ethers

3.1 Abstract

Analysis of polybrominated biphenyl ethers (PBDE) in complex environmental matrices requires a good internal standard for analyte characterization. The commonly used internal standards are fluoro-based (i.e. FBDE-69); however, their efficacy as an analytical tool has not been rigorously evaluated. In this study, a select group of new PBDE internal standards (BDE-62, BDE-118, BDE-103, and BDE-208) were used to quantify PBDEs and naturally occurring methoxy-substituted PBDEs (MeO-BDEs) from environmental standards and samples (SRM 2585 indoor dust and cod fish liver) to assess their efficacy, as well as the efficacy of FBDE-69, as internal standards for gas chromatography mass spectroscopy in electron capture negative ionization mode (GC-ECNI-MS) analysis. Internal standard calibrations were also contrasted with a control external PBDE standard calibration. Ultimately, all calibrations were compared to values produced from the standard addition method of both environmental samples. Comparison of the internal and external calibrations to the standard additions will determine the most appropriate internal standard that will identify and quantity PBDEs in the collected outdoor aerosols and fish liver samples. BDE-118 was the most appropriate internal standard for both matrix samples for both anthropogenic and natural environmentally relevant PBDEs.

3.2 Introduction

Polybrominated diphenyl ethers (PBDE) are a class of fire retardants that are banned in many jurisdictions because of their bioaccumulative and persistent properties, as well as their toxicity and ability to undergo long range transport (LRT)[1–3]. Despite these bans, monitoring of PBDEs continues to demonstrate their sustained environmental presence. This commonly entails measurement in complex matrices, often using gas chromatography coupled to mass spectrometry with electron capture negative ionization (GC-ECNI-MS). Although PBDE analysis mainly focuses on known anthropogenic sources, naturally-produced MeO-BDE congeners are also a concern. These compounds are also bioaccumulative and have the potential to convert to the more toxic OH-BDE molecular form that may emulate the thyroid hormone and may contribute to its repression[4,5].

Recently, an interlaboratory assessment of flame retardant analysis was conducted with 20 different laboratories on indoor dust extracts to evaluate the accuracy and precision of their analytical methods[6]. Accurate and precise measurements confirmed through such a study are required for the validation of environmental sample results. Sample matrix components may mask or amplify PBDE analytes during analysis with GC-ECNI-MS. In order to assist in the understanding of these matrix effects, environmental samples that will generate consistent results and have been well-characterized were needed. The National Institute of Standards and Technology (NIST) has prepared numerous standard reference materials (SRM) for various environmental matrices. Indoor dust was the first SRM characterized for PBDEs and was the most comprehensively

described matrix for organic contaminants (e.g. PBDE, polycyclic aromatic hydrocarbons, etc.) since its initial production in 2005[7].

Internal standard calibration is essential to obtaining accurate data with GC-ECNI-MS analytical methods; thus, appropriate internal standards are required. It is essential for internal standards to ionize during analysis in the same manner as the investigated analyte, since matrix effects associated with environmental samples may influence ionization efficiency and subsequently the accuracy of the results. A good internal standard must be: i) chemically similar to the analyte; ii) distinguishable from the analyte using the given method; and iii) absent from the environmental sample. These internal standards should behave like the PBDE molecule throughout the extraction and analysis processes to provide a reliable measure of analyte signal in a complex matrix. The more molecularly similar an internal standard is to an analyte, the more closely the standard mimics the analyte, and the more accurate the resulting data should be. When using MS, isotopically labelled standards are typically the most accurate internal standards. However, available isotopically labeled PBDEs contain the label on C or H atoms. The principal ionization pathway of PBDEs in ECNI is debromination leading to detection of the Br^- (m/z 79, 81) anion, which cannot be traced by these isotopically labeled PBDE standards. Frequently used internal standard for ECNI are fluoro-BDE standards, particularly 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (FBDE-69)[2,3,8–14]. As a strong electron withdrawing group, fluorine may induce a dipole onto the aromatic ring structure lowering its polarizability and its stability[15,16]. Consequently, the FBDE-69 standard, along

with its relatively high vapour pressure, is eluted at a shorter retention time than PBDEs dominant in environmental samples[9,17]. It is possible that FBDE-69 may not be the most appropriate internal standard to determine PBDE concentrations in environmental samples. A selection of chemicals from this study, including FBDE-69, were tested as internal standards for PBDE analysis by GC-ECNI-MS to assess their ability to accurately quantify anthropogenic PBDEs and MeO-BDE in complex matrices. Internal standards were used to quantify PBDEs from indoor dust and cod fish liver and the quality of the standards was assessed through comparison to standard addition calibrations.

3.3 Materials and methods

3.3.1 Internal standard selection

The internal standards (Figure 3-1) selected for this comparative study included the commonly used internal standard, FBDE-69. New internal standards included representations from the tetra-BDE (BDE-62), penta-BDE (BDE-103, BDE-118), and deca-BDE (BDE-208) classes. Congeners were selected for their similarity to PBDEs dominant in environmental samples, their lack of interference in typical GC separations, and their absence from most environmental samples.

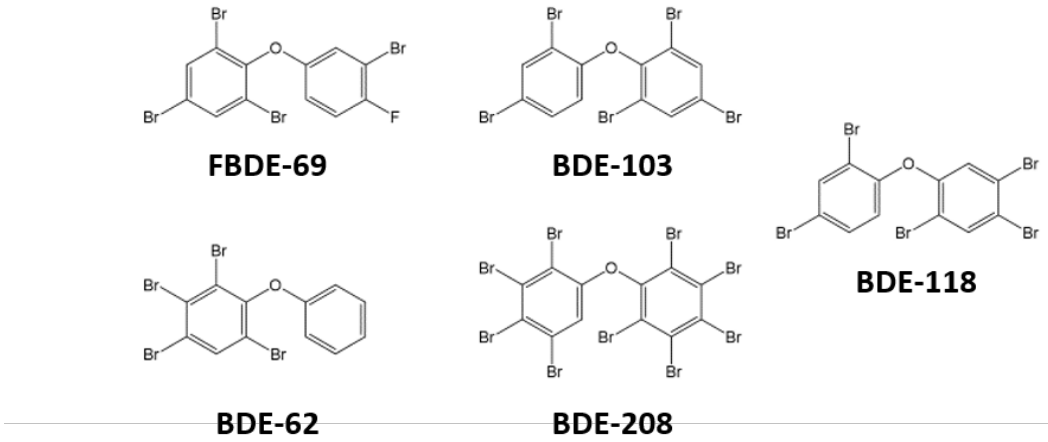

Figure 3-1. Structures of internal standards tested within this study.

3.3.2 Chemicals

Internal standards (Figure 3-1) 4'-Fluoro-2,3',4,6-tetrabromodiphenyl ether (FBDE-69), 2,3,4,6-tetrabromodiphenyl ether (BDE-62), 2,3’,4,4’,5-pentabromodiphenyl ether (BDE-118), 2,2',4,5',6-pentabromodiphenyl ether (BDE-103), and 2,2’3,3’,4,5,5’,6,6’-nonabromodiphenyl ether (BDE-208) were produced by AccuStandard Inc. (New Haven, CT, USA) and purchased from Chromatographic Specialties (Brockville, Ontario, Canada). Authentic analyte standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada): 2’,3,4’,5-tetrabromo-2-methoxydiphenyl ether (2’-MeO-BDE-68), 2,2’,4,4’-tetrabromo-5-methoxydiphenyl ether (6-MeO-BDE-47), and a suite of 27 PBDE congeners (BDE-MX) consisting of: i) 1 µL/mL of BDEs 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, and 126; ii) 2.0 µL/mL of BDEs 138, 153, 154, 156, 183, 184, 191, 196, and 197; and iii) 5.0 µL/mL of BDEs 206, 207, and 209. Toluene, acetone, and hexane (Omnisolv) solvents were acquired from VWR (Oakville, ON). The household dust (SRM 2585) was obtained from the NIST.

3.3.3 Samples and sample preparation

The cod fish liver sample was obtained on July 19, 2014 from the coastal NW Newfoundland island (49.29° N, -54.54° W) by a recreational fishing technique known as jigging (anchored hooks disguised as fish meant to catch benthic fish). The liver was extracted on site and stored at -18 °C prior to extraction. SRM dust and fish liver samples were extracted and analyzed by GC-ECNI-MS using the methods described in Chapter 2.

3.3.3.1 Standard preparation

Each internal standard (FBDE-69, BDE-62, BDE-118, BDE-103, and BDE-208) was used to produce a standard mix. Two PBDE standard stock mixes (Appendix A, Table A-1) consisting of the Wellington BDE-MX and MeO-BDE standards (6-MeO-BDE-47 and 2'-MeO-BDE-68) were produced to minimize contamination of the original stock and create a standard solution for injection. The internal standard calibration curve was created from these standard stocks in 200 µL volumes contained in GC vials (Appendix A, Table A-1). The calibration concentration range was from 0.04 µg/L and 10 µg/L, above the GC detection limit and within range of environmental PBDE concentrations. All calibration solutions and PBDE stock solutions were mixed and analytically quantified with Hamilton micro-syringes in 200 µL total volume contained in GC vials and stored at -10 °C. The SRM 2585 dust and cod fish sample were extracted and prepared for GC analysis as described in Chapter 2. All samples and calibration standards were analyzed in triplicate.

Comparable to the internal standard calibration preparation, two concentration stock solutions were diluted from the Wellington BDE-MX with toluene solvent and were

used to prepare the standard addition calibration. This standard addition calibration (Appendix A, Table A-2) consisted of six different concentrations (0, 1, 2, 5, 12.5, and 100 µg/L) of the PBDE standard concentration where toluene was used to dilute each to a total of 240 µL. All calibration solutions and PBDE stock solutions were mixed in GC inserts contained in GC vials, analytically measured with Hamilton micro-syringes (1, 10, 100, and 500 µL) and were stored at -10 °C.

3.3.3.2 Data treatment

Internal calibration curves were plotted with the dependent variable (signal peak ratio of the PBDE analyte to the internal standard signal being studied) versus the PBDE analyte concentration. Linear regression analysis was undertaken with mean peak area ratios weighted by the standard deviation of their triplicate analyses against six different concentrations of the PBDE standard concentration. Uncertainties in analyte concentrations were propagated from the uncertainties in the linear regression. External calibration curves were plotted as PBDE peak areas against PBDE analyte concentrations, where sample PBDE concentrations were calculated by linear regression. Uncertainty was assessed by propagating the error (95% confidence interval) in the calibration curves.

3.4 Results and discussion

3.4.1 Standard addition analysis of samples

Standard addition calibration compensates for matrix effects within environmental samples. This type of calibration is useful for samples with a complex matrix or when traditional calibration may not adequately represent the sample results[18]. Standard addition eliminates assumptions inherent to both external and internal calibrations, namely accurate representation of, respectively, matrix and analyte. Although standard addition is widely accepted as the most accurate calibration technique, it is rarely applied to environmental samples because of its labour and sample intensive protocols. PBDE concentrations obtained by the standard addition method were therefore assumed to be the most accurate for each sample and were compared to other calibration techniques. PBDE standard addition calibrations for the SRM house dust (Figure 3-2A) were highly linear ($R^2 \geq 0.99$). Similarly, standard additions of cod fish liver were linear ($R^2 \geq 0.99$) for the majority of the anthropogenic PBDEs (Figure 3-2B; BDEs 28, 47, 66, 99, 138, 153, 154, 183, and 184) and both natural BDEs (Figure 3-3; 6-MeO-BDE-47 and 2'-MeO-BDE-68).

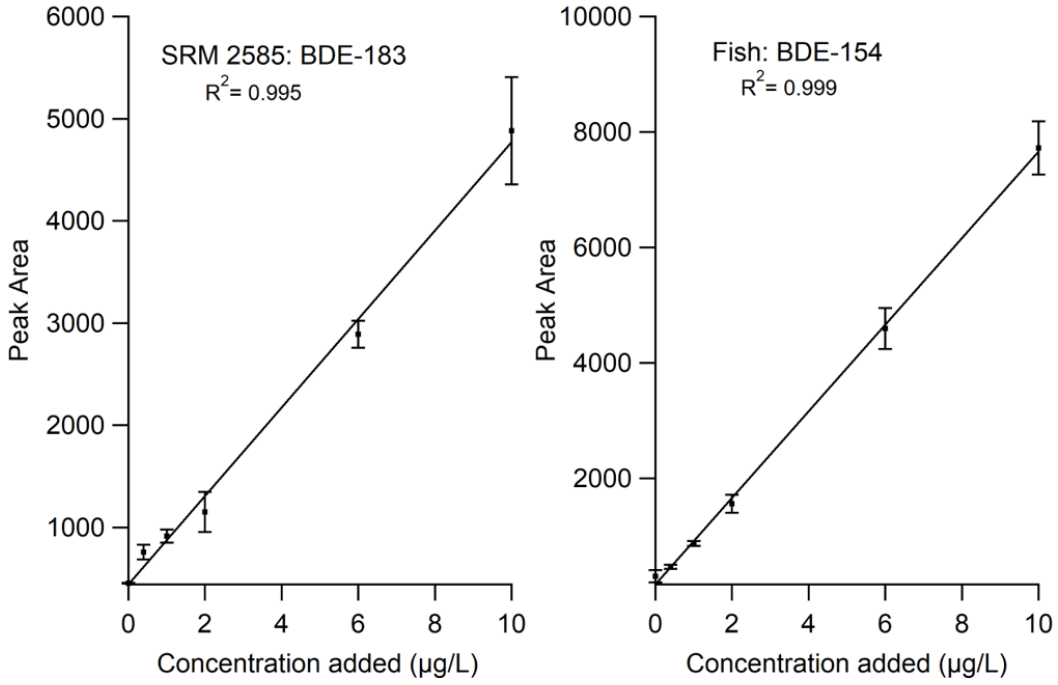

Figure 3-2. Standard addition calibrations of (a) BDE-183 in 2585 standard reference material house dust; and (b) BDE-154 in Atlantic cod fish liver. Error bars represent the standard deviation of the signal from replicate injections.

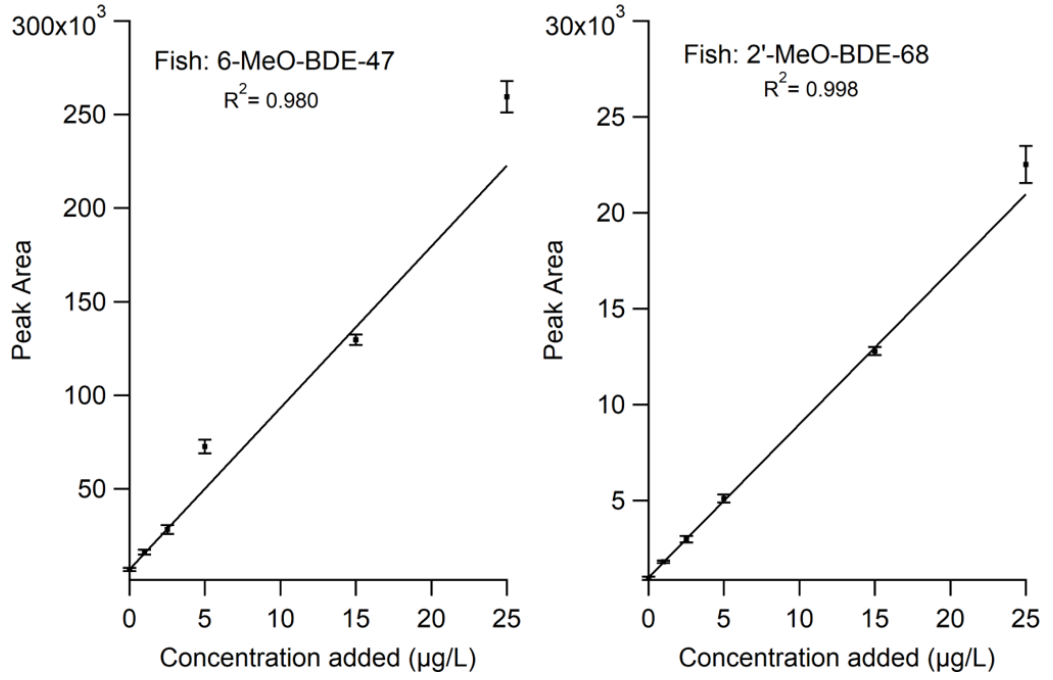

Figure 3-3. Standard addition calibrations of (a) 2’-MeO-BDE-47 and (b) 6-MeO-BDE-68 in cod fish liver sample. Error bars represent the standard deviation of the signal from replicate injections.

To provide additional confidence in the standard addition quantification, the standard addition results of both sample matrices (SRM 2585 house dust and cod fish liver) were compared with GC-ECNI-MS and gas chromatography electron ionization mass spectroscopy (GC-EI-MS) analyses reported by facilities in Gaithersburg, NIST; Charleston, NIST; and Environment Canada[19,20]. A total of 11 PBDEs (BDEs 17, 47, 66, 85, 99, 100, 153, 154, 196, 197, and 209) were compared to these reported values for SRM 2585 house dust[19,20]. Reported concentrations were determined by internal standard calibration with GC-ECNI-MS or GC-EI-MS (Table 3-1).

Methods shown in the SRM 2585 analysis (Table 3-1) from Gaithersburg, NIST facility used GC-ECNI-MS (Method A) that utilized internal standard calibration methods with (1) isotopically labeled (^{13}C) internal standards 2,2',3,4,5-pentachlorodiphenyl ether (CDE-86) and 2,3',4,4',5-pentachlorobiphenyl (PCB-118) to quantify PBDE congeners (tetra-BDEs to deca-BDEs); and (2) 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209) standard to quantify BDE-209. Environment Canada facility used GC-ECNI-MS (Method B) with CDE-86 and BDE-209 internal standards for internal standard calibration quantification. The Charleston, NIST facility used GC-EI-MS (Method C) with internal standards 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), and BDE-209 for internal standard calibration quantification. The Gaithersburg, NIST used GC-EI-MS (Method D) with internal standards BDE-99 and BDE-209 for internal standard calibration quantification. A comparison of the standard addition analyses with the reported

measurements were shown in Table 3-2. The measurements in this investigation showed reasonable agreement with reported data with the exception of BDE-66 and BDE-99.

Reported values from cod fish liver samples in this study were compared with SRM 1588b cod fish oil literature values[20]. Generally, Stapleton *et al.* (2007)[20] demonstrated greater MeO-BDE concentrations in SRM 1588b cod oil than the sampled cod fish liver from this study's results. This is likely because the whole liver tissue was assessed and did not exclusively examine the concentrated oil as with the SRM 1588b. The SRM 1588b cod fish oil sample anthropogenic PBDE analysis (Table 3-1) from Gaithersburg, NIST facility used GC-ECNI-MS (Method E) with (1) isotopically labelled internal standards 4,4-dibromodiphenyl ether (BDE-15), CDE-86, PCB-118, BDE-209, and two methoxylated PBDE standards (2'-MeO-BDE-68 and 6-MeO-BDE-47); and (2) GC-EI-MS (Method F) with internal standards BDE-99, BDE-209, 2'-MeO-BDE-68 and 6-MeO-BDE-47 for analysis. The Charleston, NIST facility used GC-EI-MS (Method G) with internal standards BDE-99 and PCB-118 for quantification[19,20]. Although GC-ECNI-MS analysis of PBDEs were monitored using ^{79}Br and ^{81}Br ions, the BDE-209 internal standard quantified BDE-209 using molecular fragments of $^{487}[C_6Br_5O]^-$ and $^{409}[C_6Br_4O]^-$; and isotopically labelled BDE-209 using $^{495}[C_6Br_5O]^-$ and $^{415}[C_6Br_4O]^-$ monitoring molecular fragments[19]. A comparison of the standard addition analyses with the reported measurements is shown in Table 3-2. In contrast to the dust, most of the measurements did not agree with reported data. Exceptions were BDEs 17, 66, and 100 with one method matching for BDE-138. Considering that SRM 1588b cod liver oil sample was intended to represent high lipid

tissue extractions and was not a direct match to the sample in this study, this disagreement is not surprising. As a comparable biotic matrix, SRM 1588b is the most suitable reference standard available to date[21].

Table 3-1. External laboratory internal calibration studies.

Sample	Method Name	Lab	Analysis Method	Internal Standards
SRM 2585	Method A	NIST (Gaithersburg)	GC-ECNI-MS	(^{13}C)CDE-86, (^{13}C)PCB-118, (^{13}C)BDE-209
SRM 2585	Method B	Environment Canada	GC-ECNI-MS	(^{13}C)CDE-86, (^{13}C)BDE-209,
SRM 2585	Method C	NIST, (Charleston)	GC-EI-MS	(^{13}C)BDE-99, (^{13}C)BDE-209
SRM 1588b	Method D	NIST (Gaithersburg)	GC-EI-MS	(^{13}C)BDE-99, (^{13}C)BDE-209
SRM 1588b	Method E	NIST (Gaithersburg)	GC-ECNI-MS	(^{13}C)CDE-86, (^{13}C)PCB-118, (^{13}C)BDE-15, (^{13}C)BDE-209, 2'-MeO-BDE-68, 6-MeO-BDE-47
SRM 1588b	Method F	NIST (Gaithersburg)	GC-EI-MS	(^{13}C)BDE-99, (^{13}C)BDE-209, 2'-MeO-BDE-68, 6-MeO-BDE-47
SRM 1588b	Method G	NIST, (Charleston)	GC-EI-MS	(^{13}C)BDE-99, (^{13}C)PCB-118

3.4.2 Evaluation of internal standards

Internal standard calibration is a commonly used analytical quantification method for samples subject to matrix effects. T-test evaluations were performed for PBDEs present in the 2585 SRM house dust sample (Table 3-2) and cod fish liver (Table 3-3) to assess the performance of the internal standards in comparison to standard addition calibration. The performance of external calibration was also tested for reference.

Table 3-2. Heat map describing PBDE concentrations in 2585 SRM house dust. Percentages indicate the difference of each calibration technique from the respective standard addition result. Colours indicate the degree of agreement: 0-25% (bold frame, light green), 26-50 % (light green), 51-100 % (dark green), > 100 % (red). Thick borders indicate that results are equivalent to standard addition results (t-test, $p < 0.05$).

	Internal calibration (%)					External calibration (%)	Stapleton *et al.* (%)			
BDE	FBDE-69	BDE-62	BDE-118	BDE-103	BDE-208		A	B	C	D
28	191	160	-17	-17	-97	-3		14	35	
47	52	35	3	77	-48	94	30	27	58	51
66	717	633	17	433	783	717	290	275	438	517
99	572	536	396	639	258	764	413	345	423	397
100	-95	-68	-79	-79	-89	-47	600	568	705	700
119	-61	-64%	-74	-56	-85	-45				
138	92	75	8	-75	17	142	1	51	17	34
153	116	100	62	93	-35	196	31	59	38	38
154	72	55	5	41	-64	116	46	56	28	27
183	161	136	54	104	-46	221	30	91	58	43
209	-20	-27	-40	44	-63	7	-12	-20	-20	

3.4.2.1 PBDEs in 2585 SRM house dust

Anthropogenic PBDEs concentrations present in 2585 SRM house dust samples were statistically evaluated (Table 3-2) to compare standard addition (Appendix B, Figure B-1) results with external standard calibration, various internal standard calibrations within this study, and internal standard calibrations in the ECNI-MS and EI-MS modes from external lab studies[19]. The 2585 SRM house dust study showed that internal standards were different ($p < 0.05$) to the standard addition method for PBDE analysis in the house dust matrix: FBDE-69 (BDEs 28, 47, 66, 85, 99, 100, 119, 153, 154, 183, 191, 196, 197, 206, 207, and 209), BDE-62 (BDEs 28, 47, 66, 85, 99, 100, 119, 153, 183, 191, 196, 197, 206, 207, and 209), BDE-118 (BDEs 28, 85, 99, 100, 119, 153, 183, 191, 196, 197, 206, 207, and 209), BDE-103 (BDEs 28, 47, 66, 85, 99, 100, 119, 153, 183, 191, 196, 197, 206, and 207),

and BDE-208 (BDEs 28, 47, 66, 85, 99, 100, 119, 183, 191, 196, 206, and 207). However, BDE-208 was able to measure ($p < 0.1$) additional PBDEs (BDEs 153, 154, and 209). The BDE-209 congener is subject to degradation at high temperatures and may bind strongly to surfaces within sample vials and the interior of analytical instruments, therefore requiring particular GC temperature programs[15,22].

A closer examination of BDE-47 (Figure 3-4), one of the most commonly found environmental anthropogenic PBDEs, demonstrated the most accurate results ($df = 4$, $p < 0.05$, t-score = 0.31) using BDE-118 internal standard in comparison to all other internal standards evaluated. In the case of tri-PBDE congeners (Figure 3-5), tetra-BDE internal standards (FBDE-69 and BDE-62) showed the poorest agreement with standard addition. In contrast, the penta-BDE internal standards (BDE-103 and BDE-118) and the external standard calibration performed much better. Considering these penta-BDE standards eluted closer to BDE-47 (tetra-BDE) in the GC chromatogram, this suggests that penta- and tetra-BDEs experience similar matrix effects. This may indicate that low-weight PBDE analytes are not as responsive to all PBDE internal standards and would suggest that the internal standards that can be used for accurate GC-MS analysis depends on similar bromination between the internal standard and its PBDE analyte. Independent t-score analysis showed that the internal standards in this study and internal standard calibrations from Stapleton *et al.* (Table 3-2) performed equivalently. The internal standards chosen for this study were more similar to the PBDE analytes than those used in the methods outlined in the Stapleton *et al.* paper and, thus, might be expected to yield better

performance. However, Stapleton *et al.* extraction procedures utlized gel permeation chromatography to extensively clean samples prior to analysis, which would eliminate matrix and reduce the likelihood of matrix effects impacting method accuracy[19]. This intensive cleaning method could account for the strong performance of chloro-based internal standards that are not as structurally similar to PBDEs as the internal standards tested here. The internal standards investigated here therefore provide equivalent performance with lower sample preparation requirements.

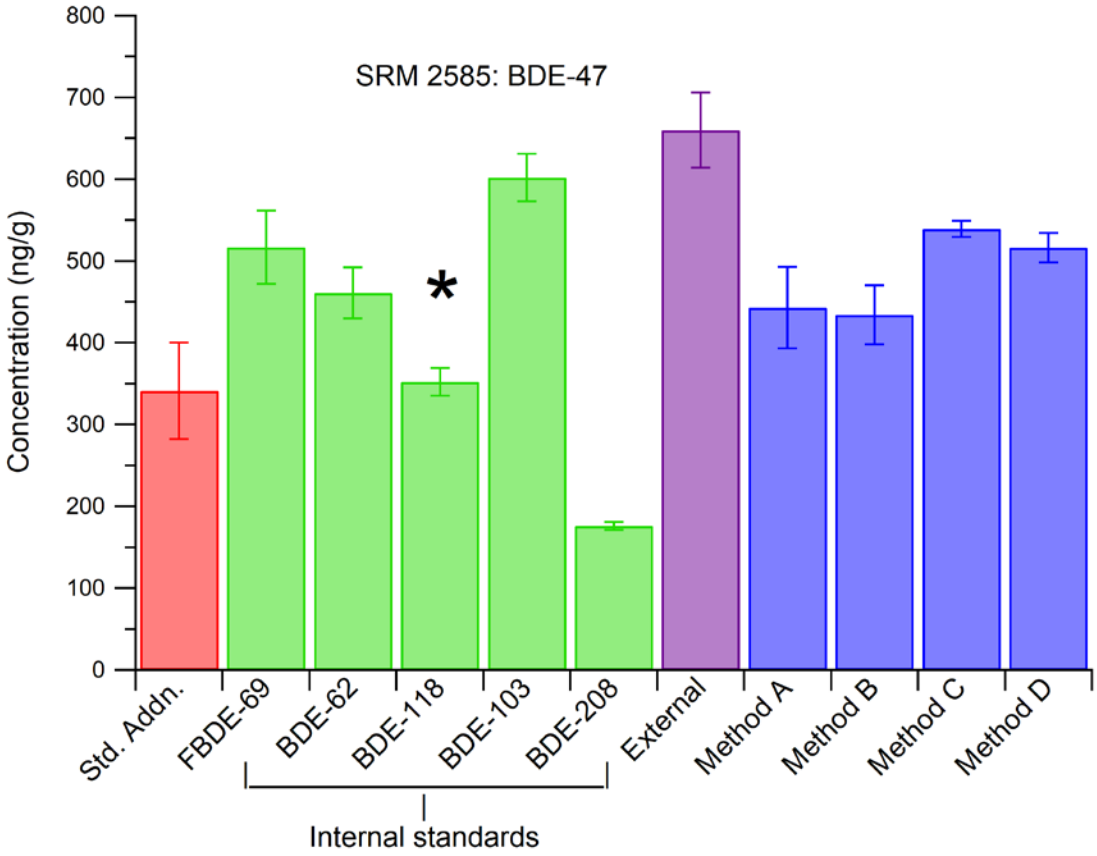

Figure 3-4. Comparison of standard addition analysis of BDE-47 in house dust 2585 standard reference material from this study and with previous external lab studies[19]. Asterisks indicate concentrations that are equivalent to standard addition concentration. Error bars represent the standard deviation of the signal from replicate injections.

Although the FBDE-69 internal standard has been widely used in the literature[2,3,8–13], this internal standard was among the standards that showed the poorest performance compared to standard addition. External standard calibration was variable throughout this study with an increasing difference from the standard addition calibration with increasing analyte bromination. Overall, BDE-118 was the internal standard best able to account for matrix effects with the greatest agreement with the standard addition method with the most PBDE analytes in this study.

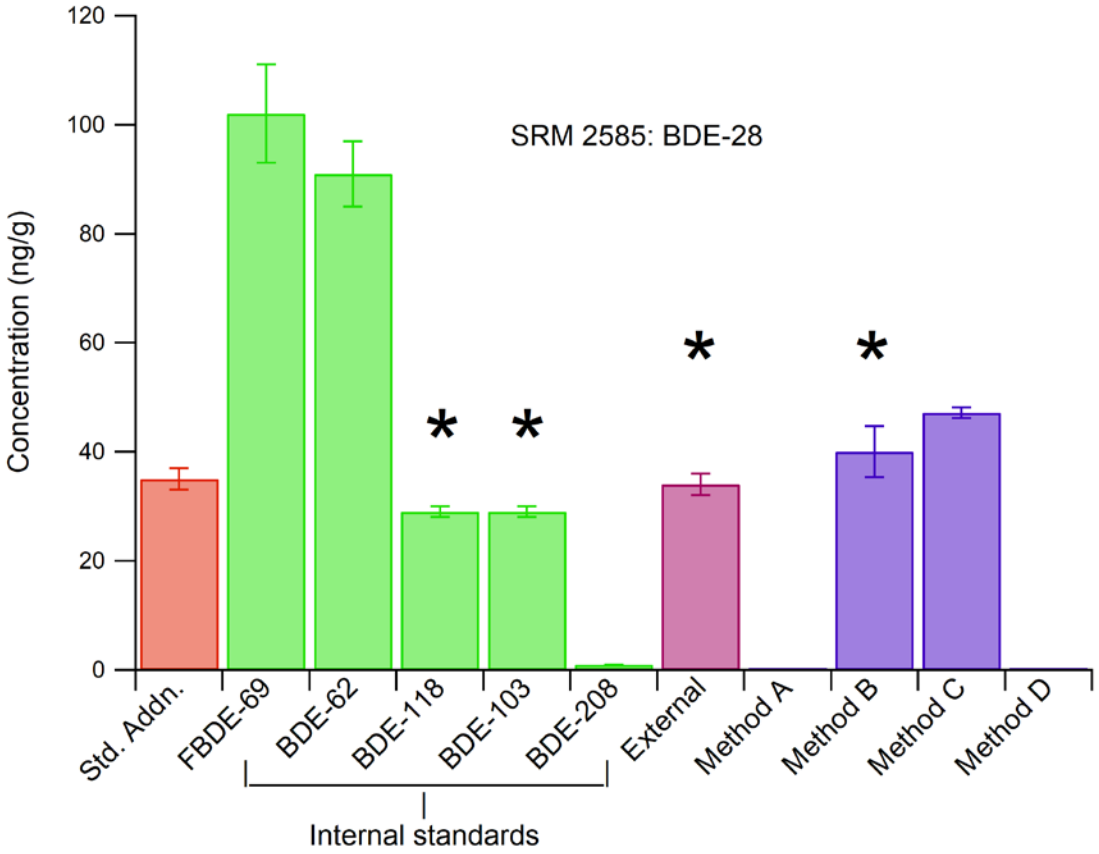

Figure 3-5. Comparison of standard addition analysis of BDE-28 in house dust 2585 standard reference material from this study and with previous external lab studies[19]. Error bars represent the standard deviation of the signal for each given GC injection for a total of 3 injections. Asterisks indicate concentrations that are equivalent to standard addition concentration.

3.4.2.2 PBDEs in cod fish

The fish liver study showed that internal standards were equivalent ($p < 0.05$) to the standard addition method for a given number of PBDEs in the cod fish matrix: FBDE-69 (6-MeO-BDE-47, 2'-MeO-BDE-68, BDEs 28, 66, and 154), BDE-62 (2'-MeO-BDE-68, BDEs 28, 66, 77, 153, and 154), BDE-118 (2'-MeO-BDE-68, BDEs 28 and 154), BDE-103 (6-MeO-BDE-47, 2'-MeO-BDE-68, BDEs 28, 47, 77, 99, and 154), BDE-208 (2'-MeO-BDE-68, BDEs 47, 77, and 99). All PBDEs found in these cod fish livers can be found in Appendix A (Figure A-2). Anthropogenic PBDEs were generally present at lower concentrations in fish than SRM house dust. This is expected considering that consumer products within indoor environments represent a point of origin for PBDEs[23,24]. External calibration generally exhibited variable agreement with the standard addition calibration because external calibration was likely influenced by sample matrix effects. Due to variable fish diet, environment, and genetics, the fish matrix may not be consistent between samples.

Table 3-3. Heat map describing PBDE concentrations in cod fish liver. Percentages indicate the difference of each calibration technique from the respective standard addition result. Colours indicate the degree of agreement: 0-25% (bold frame, light green), 26-50 % (light green), 51-100 % (dark green), > 100 % (red). Thick borders indicate that results are equivalent to standard addition results (t-test, $p < 0.05$).

	Internal calibration (%)					External calibration (%)	Stapleton *et al.* (%)		
BDE	FBDE-69	BDE-62	BDE-118	BDE-103	BDE-208		E	F	G
MeO-68	34	109	-5	-209	-118	195	108	100	-100
MeO-47	139	229	78	114	-4	395	1170	1301	-100
17	13	51	-6	51	-81	125	-99	-94	-94
28	903	1154	151	151	-25	401	183	163	211
47	17	50	0	67	-95	133	160	218	210
66	150	350	50	-50	150	571	-70	50	210
77	-110	-92	-78	-94	242	-62			-100
99	39	149	-26	387	16457	471	253	429	535
100	-100	-100	-100	-100	-100	-100	-99	-99	-99
138	40	90	-25	-440	180	140	-60	200	1960
153	100	262	99	140	630	608	-27	445	3255
154	471	676	316	364	-81	1007	30	50	18
183	-29	14	-71	-94	71	41	-86	43	410
184	-80	-76	-71	-112	114	-34			-100
191	-33	68	-184	-259	369	-38	-75	150	783

The characterization of several PBDE analytes within an environmental sample was variable between different internal standard calibrations, PBDE congeners, and environmental matrices, which suggests there may not be a single universal internal standard suitable for analysis of all PBDE congeners. Nonetheless, the heat map (Table 3-3) illustrates that the BDE-118 internal standard (Figure 3-6) is the best performing standard overall. Depending on the targeted analytes, it may be necessary to use more than one internal standard to sufficiently account for sample matrix effects and ensure accurate PBDE quantification.

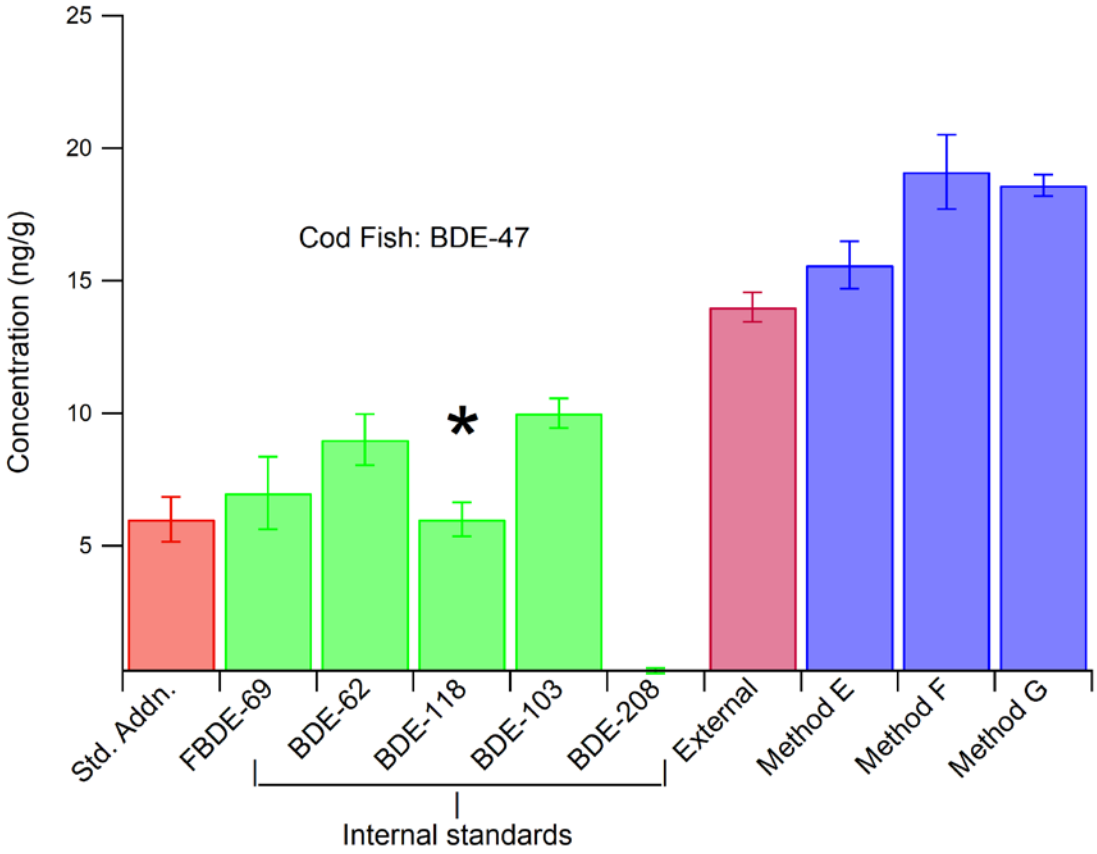

Figure 3-6. Comparison of standard addition and standard calibration analysis of BDE-47 in cod fish liver shown with reported values for SRM 1588b cod liver oil[20]. Error bars represent the standard deviation of the signal for each given GC injection for a total of 3 injections. Asterisks indicate concentrations that are equivalent to standard addition concentration.

3.4.2.3 MeO-BDEs in fish liver

MeO-BDE concentrations can vary within marine pelagic and sedimentary environments, and in the atmosphere depending on the sample matrix it is found in. Discrepancies between the measurements in this report and those of Stapleton *et al.* in Section 3.3.3.2. may be the result of environmental factors (i.e. climate, human impact, genetic pool, etc.) that could also make these particular fish samples unique to their marine region. Although internal standard calibration (Figure 3-7 and Figure 3-8) shows

variability between internal standards and standard calibrations, the FBDE-69 internal standard had the poorest agreement with the standard addition method among internal standards, suggesting that FBDE-69 will be less accurate in the presence of greater matrix and may not be an appropriate internal standard for these analytes.

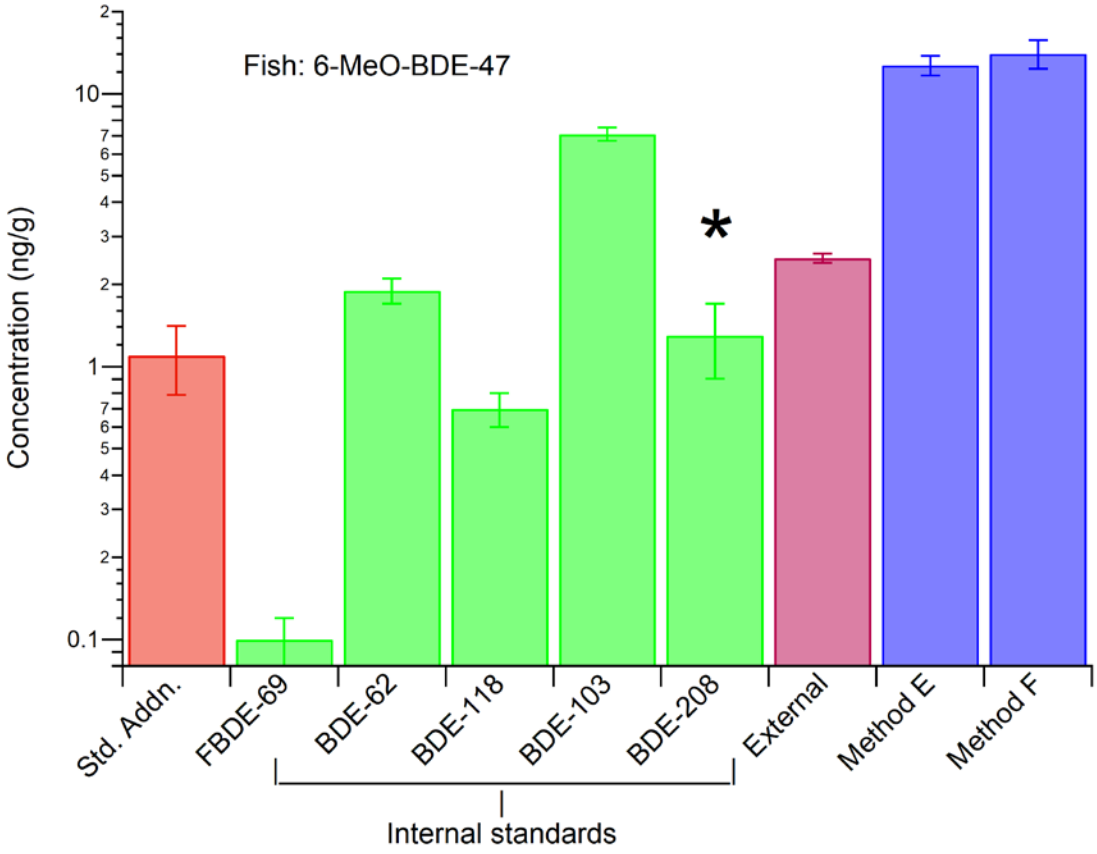

Figure 3-7. Comparison of standard addition and standard calibration analysis of 6-MeO-BDE-47 in cod fish liver shown with reported values for SRM 1588b cod liver oil[20]. Error bars represent the standard deviation of the signal for replicate injections. Asterisks indicate concentrations that are equivalent to standard addition concentration.

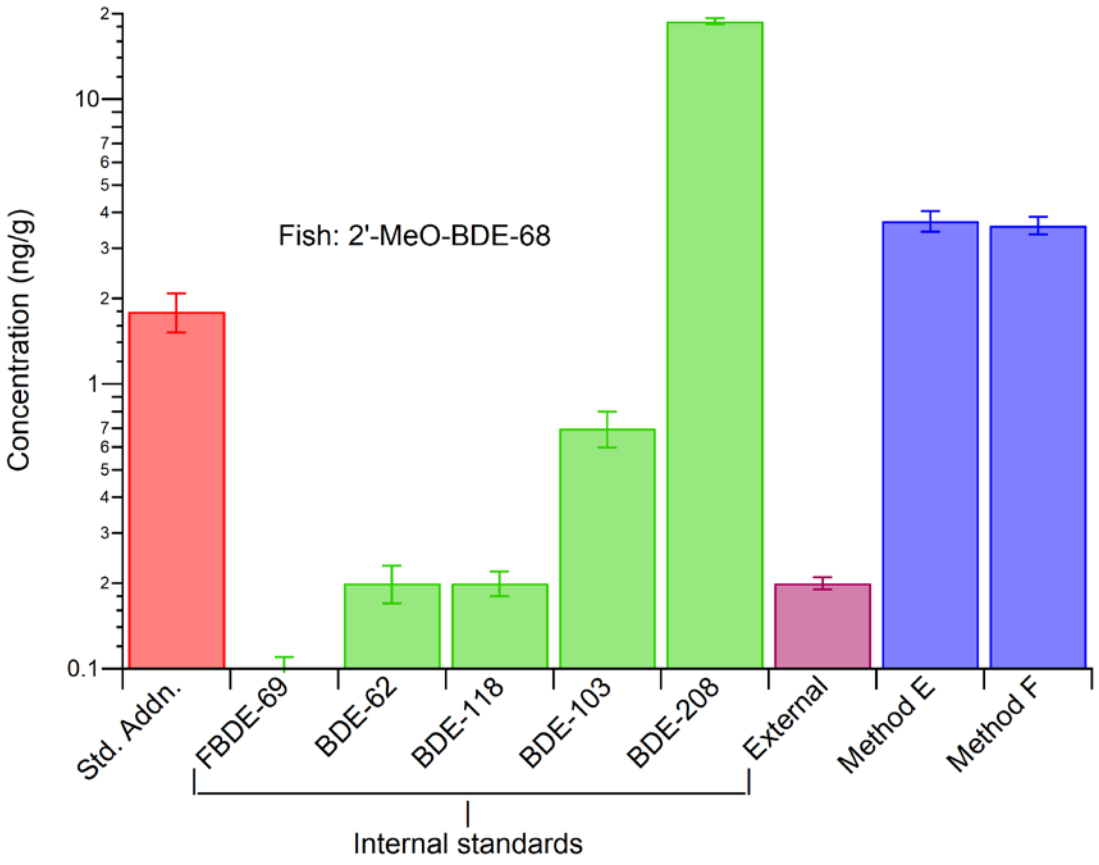

Figure 3-8. Comparison of standard addition and standard calibration analysis of 2'-MeO-BDE-68 in cod fish liver shown with reported values for SRM 1588b cod liver oil[20]. Error bars represent the standard deviation of the signal for replicate injections.

3.5 Conclusions

Sample matrices (2585 SRM household dust and cod fish liver) produced varying standard addition, internal standard, and external standard calibrations of the targeted PBDEs. An accepted practise for internal standard selection would be to pair tetra-BDE-standards with tetra-BDE-analytes; penta-BDE-standards with penta-BDEs; and highly saturated brominated PBDEs with BDE-208. In the case of the FBDE-69 internal standard, it becomes highly resolved from other PBDE analytes during GC-MS analysis as it elutes earlier than the other environmental PBDEs due to its highly electron withdrawing fluorine group. Despite this quantifiable attribute associated with FBDE-69's early retention time, this analytical trait also insulates FBDE-69 from experiencing any natural matrix effects associated with PBDEs within their characteristic retention time range, hence making FBDE-69 an inadequate internal standard for brominated flame retardants. According to Table 3-2 and Table 3-3, results showed predictable good correlation within tetra-brominated congeners with tetra-BDE-standards (FBDE-69 and BDE-62) and penta-BDE-standards (BDE-118 and BDE-103) with most of the PBDEs in the sample matrix (SRM 2585 house dust and cod fish liver), respectively. A greater lipid content may have induced a greater matrix effect in the cod fish liver sample which may explain the poorer agreement between internal standards and their respective PBDE analytes. In this case, it could be concluded that both BDE-118 and BDE-62; and perhaps BDE-103 could be viable options for internal standards because matrix effects may vary between fish and dust matrices. According to Table 3-3, FBDE-69 was equivalent to the standard addition

analysis for BDEs 17, 47, 138, 183, and 191. The accuracy of FBDE-69 with 5 PBDEs measured accurately was poorer than the accuracy achieved by the external standard calibration (6 PBDEs). Consequently, by classifying PBDE internal standard accuracy on their similar brominated content with that of their analyte, an adequate selective means of characterization may be accomplished. This study showed that internal standard performance may depend more on the complexity and type of matrix than on the degree of bromination.

Given the number of PBDE congeners and their associated environmental matrices, the internal standards of BDE-62, BDE-118, and BDE-103 were shown to have the most consistent results in relation to the standard addition calibration as the number of bromine functional groups compliments both the most and least saturated PBDE analytes. For analytically challenging highly-brominated PBDEs, notably BDE-209, BDE-208 could act as an effective internal standard[15]. However, some environmental samples may contain large quantities of BDE-208 as well as BDE-209 which would make BDE-208 an inappropriate internal standard[25]. According to Table 3-2 and Table 3-3, BDE-118 internal standard was able to accurately quantify the greatest number of PBDE analytes in both types of sample matrices (SRM 2585 house dust and cod fish liver). Of these PBDEs, important environmental PBDE analytes of anthropogenic (BDE-47) and natural MeO-BDEs (6-MeO-BDE-47 and 2'-MeO-BDE-68) were included making BDE-118 the most appropriate internal standard for continuing analyses of these PBDEs.

3.5 References

(1) Alexander, J.; Benford, D.; Boobis, A. R.; Ceccatelli, S.; Cottrill, B.; Cravedi, J. P.; Di Domenico, A.; Doerge, D.; Dogliotti, D.; Edler, L.; Farmer, P.; Filipič, M.; Fink-Gremmels, J.; Fürst, P.; Guérin, T.; Knutsen, H. K.; Machala, M.; Mutti, A.; Rose, R. Scientific Opinion on Polybrominated Diphenyl Ethers (PBDEs) in Food. *EFSA J.* **2011**, *9* (5), 1–274. https://doi.org/10.2903/j.efsa.2011.2156.

(2) Stapleton, H. M.; Sharma, S.; Getzinger, G.; Ferguson, P. L.; Gabriel, M.; Webster, T. F.; Blum, A. Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out. *Environ. Sci. Technol.* **2012**, *46* (24), 13432–13439. https://doi.org/10.1021/es303471d.

(3) Richman, K. E.; Butt, C. M.; Young, C. J. Size-Resolved Particle Measurements of Polybrominated Diphenyl Ethers Indoors: Implications for Sources and Human Exposure. *Environ. Toxicol. Chem.* **2018**, *37* (2), 481–490. https://doi.org/10.1002/etc.3981.

(4) Van Boxtel, A. L.; Kamstra, J. H.; Cenijn, P. H.; Pieterse, B.; Wagner, M. J.; Antink, M.; Krab, K.; Van Der Burg, B.; Marsh, G.; Brouwer, A.; et al. Microarray Analysis Reveals a Mechanism of Phenolic Polybrominated Diphenylether Toxicity in Zebrafish. *Environ. Sci. Technol.* **2008**, *42* (5), 1773–1779. https://doi.org/10.1021/es0720863.

(5) Weijs, L.; Losada, S.; Das, K.; Roosens, L.; Reijnders, P. J. H.; Santos, J. F.; Neels, H.; Blust, R.; Covaci, A. Biomagnification of Naturally-Produced Methoxylated Polybrominated Diphenyl Ethers (MeO-PBDEs) in Harbour Seals and Harbour Porpoises from the Southern North Sea. *Environ. Int.* **2009**, *35* (6), 893–899. https://doi.org/http://dx.doi.org/10.1016/j.envint.2009.03.006.

(6) Melymuk, L.; Diamond, M. L.; Riddell, N.; Wan, Y.; Vojta, S.; Chittim, B. Challenges in the Analysis of Novel Flame Retardants in Indoor Dust: Results of the INTERFLAB 2 Interlaboratory Evaluation. *Environ. Sci. Technol.* **2018**, *52*, 9295−9303. https://doi.org/10.1021/acs.est.8b02715.

(7) Bergh, C.; Luongo, G.; Wise, S.; Östman, C. Organophosphate and Phthalate Esters in Standard Reference Material 2585 Organic Contaminants in House Dust. *Anal. Bioanal. Chem.* **2012**, *402* (1), 51–59. https://doi.org/10.1007/s00216-011-5440-2.

(8) Klösener, J., Peters, T. M., Adamcakova-Dodd, A., Teesch§, L., Thorne, P. S., Robertson, L.W., Luthe, G. Innovative Application of Fluoro-Tagging to Trace Airborne Particulate and Gas Phase PBDE Exposures. *Chem Res Toxicol.* **2009**, *22* (1), 179–186. https://doi.org/10.1016/j.micinf.2011.07.011.Innate.

(9) CHIRON. BMF 15 - Polybrominated Diphenylethers (PBDEs) and Other Flame Retardants, 2012.

(10) Leonetti, C.; Butt, C. M.; Hoffman, K.; Miranda, M. L.; Stapleton, H. M. Concentrations of Polybrominated Diphenyl Ethers (PBDEs) and 2,4,6-Tribromophenol in Human Placental Tissues. *Environ. Int.* **2016**, *88*, 23–29. https://doi.org/10.1016/j.envint.2015.12.002.

(11) Hammel, S.; Phillips, A.; Hoffman, K.; Stapleton, H. M. Evaluating the Use of Silicone Wristbands to Measure Personal Exposure to Brominated Flame Retardants. *Environ. Sci. Technol.* **2018**, *52* (20), 11875–11885. https://doi.org/10.1021/acs.est.8b03755.

(12) Marler, H.; Adams, D. H.; Wu, Y.; Nielsen, C. K.; Shen, L.; Reiner, E. J.; Chen, D. Maternal Transfer of Flame Retardants in Sharks from the Western North Atlantic Ocean. *Environ. Sci. Technol.* **2018**, *52* (22), 12978–12986. https://doi.org/10.1021/acs.est.8b01613.

(13) Tang, S.; Tan, H.; Liu, X.; Chen, D. Legacy and Alternative Flame Retardants in House Dust and Hand Wipes from South China. *Sci. Total Environ.* **2019**, *656*, 1–8. https://doi.org/10.1016/J.SCITOTENV.2018.11.369.

(14) Wu, Y.; Tan, H.; Zhou, C.; Crimmins, B. S.; Holsen, T. M.; Pagano, J. J.; Chen, D. Spatial and Temporal Trends (2004 – 2016) of Selected Alternative Flame Retardants in Fish of the Laurentian Great Lakes. *Environ. Sci. Technol.* **2019**, *53* (4), 1786–1796. https://doi.org/10.1021/acs.est.8b05300.

(15) Stapleton, H. M. Instrumental Methods and Challenges in Quantifying Polybrominated Diphenyl Ethers in Environmental Extracts: A Review. *Anal. Bioanal. Chem.* **2006**, *386* (4), 807–817.

(16) Liu, H.; Skålvoll, A.; Reijerink, G. S.; Luthe, G.; Johansen, J. E. Synthesis of Fluorinated Polybrominated Diphenyl Ethers (F-PBDEs) as Internal Standards for Environmental Analysis. *Chemosphere* **2006**, *64* (2), 250–255. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2005.12.010.

(17) Liu, H.; Bernhardsen, M.; Fiksdahl, A. Polybrominated Diphenyl Ethers (BDEs); Preparation of Reference Standards and Fluorinated Internal Analytical Standards. *Tetrahedron* **2006**, *62* (15), 3564–3572. https://doi.org/http://dx.doi.org/10.1016/j.tet.2006.01.092.

(18) Brown, R. J. C.; Webb, W. R.; Goddard, S. L.; Kim, K.-H.; Blakley, K. C. Exact Matching Strategies for Generalised Sequential Standard Addition Calibration. *Anal. Methods* **2014**, *6* (1), 102. https://doi.org/10.1039/c3ay41567h.

(19) Stapleton, H. M.; Harner, T.; Shoeib, M.; Keller, J. M.; Schantz, M. M.; Leigh, S. D.; Wise, S. A. Determination of Polybrominated Diphenyl Ethers in Indoor Dust Standard Reference Materials. *Anal. Bioanal. Chem.* **2006**, *384* (3), 791–800. https://doi.org/10.1007/s00216-005-0227-y.

(20) Stapleton, H. M.; Keller, J. M.; Schantz, M. M.; Kucklick, J. R.; Leigh, S. D.; Wise, S. A. Determination of Polybrominated Diphenyl Ethers in Environmental Standard Reference Materials. *Anal. Bioanal. Chem.* **2007**, *387* (7), 2365–2379.

(21) Wise, S. A.; Poster, D. L.; Kucklick, J. R.; Keller, J. M.; Vanderpol, S. S.; Sander, L. C.; Schantz, M. M. Standard Reference Materials (SRMs) for Determination of Organic Contaminants in Environmental Samples. *Anal. Bioanal. Chem.* **2006**, *386* (4), 1153–1190. https://doi.org/10.1007/s00216-006-0719-4.

(22) Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A. Novel Brominated Flame Retardants: A Review of Their Analysis, Environmental Fate and Behaviour. *Environ. Int.* **2011**, *37* (2), 532–556. https://doi.org/10.1016/j.envint.2010.11.007.

(23) Law, R. J.; Covaci, A.; Harrad, S.; Herzke, D.; Abdallah, M. A.-E.; Fernie, K.; Toms, L.-M. L.; Takigami, H. Levels and Trends of PBDEs and HBCDs in the Global Environment: Status at the End of 2012. *Environ. Int.* **2014**, *65*, 147–158.

(24) Zhang, X.; Diamond, M. L.; Robson, M.; Harrad, S. Sources, Emissions, and Fate of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls Indoors in Toronto, Canada. *Environ. Sci. Technol.* **2011**, *45* (8), 3268–3274. https://doi.org/10.1021/es102767g.

(25) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-Retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254. https://doi.org/10.1021/es060630m.

4 Analysis of polybrominated diphenyl ethers in size-resolved atmospheric aerosol samples

4.1 Abstract

Polybrominated diphenyl ether (PBDE) long range transport (LRT) in the atmosphere through aerosols is poorly understood. With the recent discovery of atmospheric MeO-BDE, these environmental contaminants and PBDEs may have a greater potential for global exposure than expected. The utilization of the micro orifice uniform deposition impactor (MOUDI) to collect aerosols based on their aerodynamic diameter would infer their sources, probable distance of travel, and PBDE exposure. Aerosol samples were collected on a rooftop at Memorial University of Newfoundland, in St. John's. Higher PBDE concentrations collected during warmer summer seasons demonstrated a trimodal aerosol pattern in the coarse, fine, and ultrafine aerosol modes. The presence of MeO-BDE (trace levels below the limit of detection (LOD) to 0.969 pg/m^3) and BDE-209 (below LOD to 23.6 pg/m^3) in the fine aerosol mode demonstrated potential for aerosol-mediated LRT. To our knowledge, this is the first study to measure MeO-BDEs in size-resolved aerosols. Anthropogenic ∑PBDE levels (1.05 – 12.5 pg/m^3 without BDE-209) were greater than MeO-BDE congeners throughout the year and experienced similar seasonal aerosol collection patterns. No significant correlations between MeO-BDE aerosol loadings and wind speed, temperature, or $PM_{2.5}$ abundance was shown. This suggests that MeO-BDE levels may not necessarily coincide with primary production and may be a product of local indoor/outdoor household aerosol interactions and LRT from the summer Canadian mainland and winter Atlantic Ocean marine air.

4.2 Introduction

The environmental release of polybrominated diethyl ethers (PBDE) through their use as commercial fire retardants has become a health concern. With a similar molecular structure to thyroid hormone, PBDEs have the capacity to compete for endocrine binding sites and inhibit these pathways[1–4]. Although the manufacturing of PBDEs has been banned for over a decade[5,6], PBDEs still represent a substantial fraction of the total environmental load of persistent organic pollutants (POPs)[7,8]. Common natural congeners of methoxy (MeO-BDE) and hydroxy (OH-BDE) congeners and their bromoanisole (BA) precursors (2,4-di-BA and 2,4,6-tri-BA) are predominately produced from phytoplankton (e.g. cyanobacteria and red algae), sponges (*Dysidea* sp.), and blue mussels (*Mytilus edulis*) and are present at similar concentrations as PBDEs in the marine environment[9–20]. Measurements of natural PBDE analogues in non-marine media are rare and the propensity for these compounds to undergo long range transport (LRT) is uncertain.

There are only a few aerosol aerodynamic size distribution studies (Table 4-2) conducted in open marine environments, some of which have the PBDE analyte as a research focus[21–25]. These collections were accomplished by various types of atmospheric samplers. Sampler setups consisted of numerous independent size selective particulate matter (PM) filters (1 µm, 2.5 µm, 10 µm: PM_1, $PM_{2.5}$, PM_{10} respectively), dichotomous particulate samplers, and polyurethane foam (PUF) disk passive air sampler to collect differing aerosol diameters for a given collection event[25–33]. Total suspended particles (TSP) were commonly used to monitor atmospheric PBDEs (Table 4-1). Health studies

usually collected particulate matter less than 2.5 μm in diameter ($PM_{2.5}$) since $PM_{2.5}$ are able to enter the blood stream through the alveoli within mammalian lungs and represent a potential health concern[34–40]. Alternatively, cascade compactors (4 – 8 substrate stages) were used for POPs studies as a single stream aerosol collection system for a consistent sample collection and more dynamic range of aerodynamic aerosol size collection[21,22,24,41–44]. The introduction of the micro orifice uniform deposit impactor (MOUDI) setup was an innovative improvement with monitored stream flow to minimize sample blow-off. The first MOUDI iteration for PBDE collection was a 11-stage micro range aerosol setup[45–48]. Pham *et al.* utilized a 10-stage MOUDI setup to speciate organic content in collected sea spray aerosols. A newer 14-stage (< 100 nm) MOUDI model was designed for nano aerosol collection[49]. This 14-stage MOUDI system has been used to measure PBDEs in size-resolved aerosols in only three studies: indoors[50], outdoor aerosols produced from thermal treatment of e-waste[51], and on haze in China as a mechanism for enhanced exposure[45]. To our knowledge, MeO-BDEs have never been detected in size-resolved aerosols. In this study, marine aerosols based on their aerodynamic diameter from a coastal urban region in Newfoundland (NL), Canada were collected. PBDEs and MeO-BDEs were measured in these aerosol samples to: i) assess sources of aerosol PBDE and MeO-BDE as a function of season; and ii) determine the likelihood of aerosols contributing to LRT for these compounds.

Table 4-1. Selected PBDE measurements in total suspended particles (TSP) aerosols.

Location	Sampling Year	∑PBDE	∑[PBDE] pg/m^3	Reference
Northern Baltic Sea	2015-2012	2′-MeO-BDE-68, 6-MeO-BDE-47	2′-MeO-BDE-68: Avg. 0.017 ± 0.016, 6-MeO-BDE-47: Avg. 0.014 ± 0.011	[19]
Canadian Western Sub-Arctic	2014-2011	$\sum_{14}$PBDE: BDEs 17, 28, 47, 49, 71, 66, 100, 99, 85, 153, 154, 138, 183, 190	Range 0.42 - 18, Avg. 1.6	[52]
Chinese Great Wall Station, West Antarctic	2014-2011	$\sum_{16}$PBDE: BDEs 15, 17, 28, 47, 99, 100, 138, 153, 154, 183, 184, 196, 197, 206, 207, 209	Range 0.60 - 16.1, Avg. 3.28 ± 3.31	[53]
Canadian Western Sub-Arctic	2014-2011	$\sum_{6}$PBDE: BDEs 17, 28, 49, 71, 47, 66, 100, 99, 85, 154, 153, 138, 183, 190	Range 0.42 - 18, Avg. 1.6	[19]
North Greenland	2013-2008	$\sum_{6}$PBDE: BDEs 17, 28, 47, 71, 99, 100	Range 0.20 - 6.26	[54]
Toolik Lake, Arctic	2013	$\sum_{12}$PBDE: BDEs 17, 28, 47, 66 71, 85, 99, 100, 138, 153, 154, 183, 209	Avg. 2.9 ± 5.5, 2.5 ± 3.8, 0.5 ± 0.8	[55]
Longyearbyen, Arctic	2013-2012	$\sum_{35}$PBDE: BDEs 7, 10, 17, 28, 30, 47, 49, 66, 71, 85, 99, 100, 119, 126, 138−140, 153, 154, 156, 169, 180, 183, 184, 191, 196, 197, 201, 203−209	Avg. 5.6 ± 1.1	[56]
Lake Erie	2012-2011	$\sum_{12}$PBDE: BDEs 2, 8, 15, 30, 28, 47, 49, 100, 99, 153, 154, 183	11	[57]
Southern Ocean	2011-2010	$\sum_{10}$PBDE: BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183, 209	0.13	[58]
Atlantic Ocean, North Sea	2010	$\sum_{6}$PBDE: BDEs 47, 99, 100, 153, 183, 209	Range 0.31−10.7	[59]

Table 4-1 (cont'd). Selected PBDE measurements in total suspended particles (TSP) aerosols.

Location	Sampling Year	∑PBDE	∑[PBDE] pg/m^3	Reference
Arctic Ocean	2010	$\sum_{10}$PBDE: BDEs 28, 47 ,66, 85, 99, 100, 153, 154, 183, 209	Range 0.06 - 1.6, 0.03 - 0.46	[60]
Busan, South Korea	2010	$\sum_{27}$PBDE: BDEs 3, 7, 15, 17, 27, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209 $\sum_{18}$MeO-BDE: 3'-MeO-BDE-28, 5-MeO- BDE-47, 6-MeO-BDE-47, 4-MeO-BDE-49, 2-MeO-BDE-68, 5'-MeO-BDE-99, 5-MeO-BDE-100, 4'-MeO-BDE-101, 4-MeO- BDE103, eight tri- to penta-brominated MeO-BDEs, one unidentified tri-brominated MeO-BDE $\sum_{45}$OH-BDE: 3'-OH-BDE-28, 6-OH-BDE-47, 6-OH-BDE-100, six tri- to penta-brominated OH-BDEs, one unidentified tri-brominated OH-BDE	$\sum_{27}$PBDE: 5.3 – 16 $\sum_{18}$MeO-BDE: 15 – 87 $\sum_{10}$OH-BDE: > DL	[61]
North Sea	2010	$\sum_{10}$PBDE: BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183, 209	0.07 - 8.1	[59]
George Island, Antarctica	20010-2009	$\sum_{14}$PBDE: BDEs 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	0.67 - 2.98	[62]
West Antarctic Peninsula	2010	$\sum_{12}$PBDE: BDEs 2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 154, 183	Avg. 4.2, (1.4 - 7.6)	[63]
Atlantic Ocean (Namibia via Barbados)	2009	$\sum_{7}$PBDE: BDEs 66, 100, 99, 154, 153, 183, 209	PBDE (< 0.1), BDE-209: Median 1.2, BDE-99: Avg. 0.13	[64]
East Greenland Sea	2009	$\sum_{10}$PBDE: BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183, 209	0.09 - 1.8	[65]

Table 4-1. (cont'd) Selected PBDE measurements in total suspended particles (TSP) aerosols.

Location	Sampling Year	∑PBDE	∑[PBDE] pg/m^3	Reference
Atlantic Ocean	2008	$\sum_{21}$PBDE: BDEs 17, 28, 32, 35, 37, 47, 49, 51, 66, 71, 75, 77, 99, 100, 126, 128, 138, 153, 154, 166, 183	2.87 ± 1.81	[66]
Atlantic Ocean	2008	$\sum_{9}$PBDE: BDEs 28, 47, 66, 85, 99, 100, 153, 154, 183	Avg. 0.33 (< 0.04 - 2.16) North: Range 0.65 - 3.30, South: Range 0.40 - 1.33	[37]
Alert, Nunavut, Canadian Arctic	2008-2007	$\sum_{5}$PBDE: BDEs 47, 99, 100, 153, 209	Avg. 3.8 (median 1.2 - 55)	[36]
Great Lakes	2006-2005	$\sum_{35}$PBDE: BDEs 1, 3, 7, 10, 15, 17, 28, 30, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 139, 140, 153, 154, 156, 169, 171, 181, 183, 184, 191, 196, 197, 201, 203-209	Avg. 5.8 ± 0.4	[67]
Nuuk, West Greenland	2005 & 2004	$\sum_{11}$PBDE: BDEs 17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 183	Avg. 1.14 ± 0.81	[68]
Alert, Nunavut, Canadian Arctic	2004–2002	$\sum_{15}$PBDE: BDEs 17, 28, 49, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, 190, 209	Range 0.78 - 48, and 0.40 - 47	[69]
Arctic Ocean	2003	$\sum_{11}$PBDE: BDEs 28, 47, 66, 100, 99, 85, 138, 153, 154, 153, 138, 183, 209	15.2	[70]
Macehead, Ireland	2000	$\sum_{21}$PBDE: BDEs 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 166, 181, 190	2.6	[71]

*DL = detection limit

4.3 Materials and methods

Analytical standards and chemicals were purchased as described in Chapter 2. Analyte extractions and gas chromatography mass spectroscopy (GC-MS) analysis were performed as described in Chapter 2.

4.3.1 Aerosol collection

Sampling was conducted on the rooftop of Memorial University (MUN) Alexander Murray Building as part of the Memorial University Atmospheric Sampling Site (MURASS, 47.575° N, 52.734° W, 58 m above sea level). A MOUDI sampler was set up for aerosol collection with a constant air inflow (30 L/min) that was supplied by an external vacuum pump (MDI-122-0040, MSP Corp.). Aerosols were systemically sorted by their aerodynamic diameter from larger to progressively smaller aerosol sizes and collected over 14 consecutive substrate stages (numbered 0 – 13 stages; 0 stage is the inlet stage). The aerodynamic diameter range of these substrate stages for aerosols entering and flowing through the setup is from 18 µm to 10 nm. Seven samples were collected over the period from August 2015 to October 2016 (Table 4-2). Each sample was collected over approximately 30 d. Most samples were collected between late spring and early fall. Only one sample was collected in the winter because of logistical challenges associated with sample collection during winter weather.

The MOUDI size fractions aerosols by limiting their trajectory paths with designated impacts to the quartz fiber filters (QFF) between each collection stage. The aerosol critical trajectory of each sampling stage is manipulated with decreasing entry

openings and stage proximity to these openings as stages collect progressively smaller and smaller aerosols the further, they travel down the setup. Larger aerosols that cannot bypass this critical trajectory become impacted, whereas smaller aerosols follow the air flow to the next chamber. PBDE loadings were only reported for aerosols on the twelve stages between 10 nm and 10 µm (i.e. stages 2 to 13).

Table 4-2. Dates and durations of size-resolved aerosol sample collection from 2015-2016.

Sample Number	Sample Start Date	Sample End Date	Duration (h)
1	July 28 2015	Aug. 24, 2015	641.3
2	Aug. 24, 2015	Nov. 8, 2015	905.3
3	Jan. 27, 2016	Feb. 29, 2016	791.3
4	May 31, 2016	June 29, 2016	691.5
5	June 30, 2016	Aug. 1, 2016	671.0
6	Aug. 2, 2016	Sept. 7, 2016	860.5
7	Sept. 9, 2016	Oct. 7, 2016	682.3

MOUDI aerosols were collected on QFF substrates that were pre-baked for at least 4 hours at 500 °C. Substrates were stored at 10 °C after being conditioned in new polystyrene petri dishes (47 mm and 90 mm). Extraction and analysis procedures were performed as described in Chapter 2. Seasonal environmental parameters ($PM_{2.5}$ abundance, regional temperature, and wind speed data) were obtained for MOUDI sampling periods. The $PM_{2.5}$ data (January 2015 - December 2016) was acquired from the National Air Pollution Surveillance (NAPS) Station (Gentara Building, St. John's, NL), approximately 2 km southeast of the sampling site. Temperatures and wind speed (2015 - 2016) data sets were reported at St. John's International Airport approximately 5 km north of the sampling site[72].

4.3.2 Air mass back trajectories

Air mass origins were performed with National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model from a single field site[73–75]. Back trajectories were performed for each sample period using the global data assimilation system (GDAS) meteorology data. Back trajectories were initiated at ground level every 3 hours for the duration of the sampling period (~30 days) with each back trajectory running for 120 hours. Frequency plots set at 0.5-degree resolution was generated with the NOAA HYSPLIT online interface to geographically represent air mass histories.

4.3.3 Quality assurance and quality control

All PBDE quantification was accomplished by internal calibration using BDE-118 as an internal standard. Instrumental GC-MS variability was accounted for by triplicate GC injection. After sample clean-up and blow-down to ~250 µL, 1.5 µL aliquots of a 2 mg/L solution of BDE-118 was added to each sample prior to GC-MS injection. No PBDEs were detected in analytical blanks consisting of toluene. Analytical limits of detection and limits of quantification were calculated as three and ten times the signal-to-noise ratio of the analytical blank, respectively. Method detection limits were calculated with pre-baked QFF filter field blanks briefly exposed to the ambient environment at the start of each MOUDI sample collection as three times the standard deviation of the blank. Signals observed in method blanks (consisting of solvent taken through the extraction process) were subtracted from the extracted analytes to account for unavoidable contamination

during the extraction process. The accuracy of the method was confirmed by analysis of National Institute of Standards and Technology (NIST) 2585 house dust standard reference material as described in Chapter 3.

4.4 Results and discussion

4.4.1 Aerosol PBDE concentrations

Observations of ∑PBDEs in aerosols at a range of 1.05 – 12.5 pg/m^3 (without BDE-209) were found at our urban sampling site on a rooftop at Memorial University. PBDEs were detected in all sampling periods with concentrations as follows: BDE-209 > BDE-28 > BDE-47 > BDE-99 > 2'-MeO-BDE-68 > 6-MeO-BDE-47. Since detection limits were higher for BDE-209 (0.2496 – 23.60 pg/m^3) in this method, it was detected in fewer samples (4/7 sampling periods), similar to other studies in Table 4-3[76,77]. However, when it was detected, it was representative of a large proportion of the PBDEs present.

Studies have shown a trend in greater PBDE concentrations within dense urban cities compared to adjacent rural areas and more remote regions[22,26,44,55,78]. Metropolitan hubs are sources of human consumption and production of these PBDE consumer products (e.g. computers and furniture)[21,41,46,78–80]. All sample sites in this study are considered urban with observations that are comparable to, but on the low end of, measurements in other marine locations (Table 4-2 and Table 4-3), including the North Atlantic marine boundary layer (2008), Mace Head (Ireland, 2000-2001), Alert (NU, Canada, 2002-2004), and Busan (South Korea, 2010). Owing to the manufacturing ban of PBDEs imposed by global environmental regulations, aerosol samples collected from

Europe and world wide have recorded lower concentrations of anthropogenic PBDEs within the last decade[30]. Lower observed aerosol PBDEs from these reported cities ranged from 0.2 – 47 pg/m^3 that primarily consists of BDE-47, BDE-99, and BDE-209[29,37,58,65,69,71,76,81]. As a major component in the penta-BDE MX and a degradative intermediate of BDE-209, BDE-47 is normally the dominant congener in aerosol samples with a relatively high vapor pressure (1.40 x 10^{-6} mm Hg)[80]. Wang *et al.*[53] measured aerosol BDE-209 at 0.18 - 6.35 pg/m^3 at the Great Wall station, West Antarctica. It has also been measured at 1.0 ± 1.6 pg/m^3 in the Arctic[55].

Measurements of semi volatile organic compounds (SVOCs), such as PBDEs, may experience sampling artifacts during sampling, caused primarily by gas-particle partitioning[82]. Blow-off artifacts have been shown to lead to analyte loss from impactor samplers[48,83–85]. Analyte loss may be attributed to the difference in analyte concentrations between the sampling chamber gas phase and the collected solid phase; and the pressure drop between sampler chamber compartment and the immediate surface of the collection substrate. Therefore, SVOC loss by evaporation or air flow blow-off could be minimized within aerosol impactors under these criteria: (1) constant temperature; (2) constant gas phase and aerosol concentrations; and (3) analyte at equilibrium between gas phase and aerosols. Variable weather and diurnal temperature changes incurred through long-term sampling may create losses greater than 10% in impactors[86]. Although impactor samples may consistently have blow-off effects and sample loss through evaporation that cannot be completely eliminated, MOUDI impactors, such as the sampler

used here, minimize these losses through a controlled pressure drop[21,22,24,44,47,48,86]. Since an instrument was used with demonstrated minimal blow-off, and because measurements are similar in magnitude to other atmospheric sampling methods, it was argued that these PBDE MOUDI results are acceptable and reliable[22,48,87]. It was noted that blow-off effects are larger in magnitude for smaller aerosols. Richman *et al*.[50] estimated potential blow-off effects for this MOUDI sampler, demonstrating that blow-off effects were negligible for aerosols larger than 100 nm. Below that size, blow-off effects increased as aerosol size decreased, from ~20 % (0.56 to 100 nm size fraction) to ~60 % (10 to 18 nm size fraction)[48]. Therefore, this examination may have been underestimating the PBDEs and MeO-BDEs in aerosols 100 nm and smaller[50]. Errors are included to account for the theoretical maximum blow-off[86].

Table 4-3. Selected PBDE measurements in size-resolved aerosols.

Location	Sampling Year	Aerosol Type	∑PBDE	∑[PBDE] pg/m^3	Reference
St. John's, Canada	2016, 2015	0.010, 0.018, 0.032, 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10, 18 mm	$\sum_4$PBDE: BDEs 28, 47, 99, 209, 2'-MeO-BDE-68, 6-MeO-BDE-47	$\sum_4$[PBDE]: 1.59 - 2.41 $\sum_2$[MeO-BDE]: 0.0593 - 2.39	This study
St. John's, Canada	2015, 2014	0.010, 0.018, 0.032, 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10, 18 mm	$\sum_5$PBDE: BDEs 47, 99, 100, 183, 209	Indoors: 8.7 ± 0.5 - 15.7 ± 0.5	[48]
Thessaloniki, Northern Greece	2013	< 0.49, 0.49-0.97, 0.97-1.5, 1.5-3.0, 3.0-7.2, > 7.2 µm	$\sum_{12}$PBDE: BDEs 15, 17, 28, 49, 71, 47, 66, 99, 100, 153, 154, 183	Traffic: 20.3 Urban: 27.1	[21]
Neochorouda and Finokali (Greece)	2012	< 0.95, 0.95 –1.5, 1.5 – 3.0, 3.0 – 7.2, > 7.2 µm	$\sum_7$PBDE: BDEs 28, 47, 66, 99, 100, 153, 154, 209	$\sum_7$PBDE: 0.95, BDE-209: 0.81	[41]
Guangzhou, China	2010	< 0.056, 0.056−0.1, 0.1−0.18, 0.18−0.32, 0.32−0.56, 1−1.8, 1.8−3.2, 3.2−5.6, 5.6−10, 10− 18, and > 18 µm	$\sum_4$PBDE: BDEs 47, 99, 183, 207, 209	Avg. 745 (400 - 1300)	[46]
Athens, Heraklion, Finokalia, (Greece)	2007 2006	A. Greece: > 8.10, 8.10 – 3.36, 3.36 – 1.66, 1.66 – 1.08, 1.08 – 0.57, < 0.57 µm, 0.21 µm; H. and F. Greece: 0.14 – 0.63 µm	$\sum_{12}$PBDE: BDEs 15, 17, 28, 47, 49, 62, 71, 99, 100, 153, 154, 183	Heraklion: $\sum_{12}$PBDE: 4 – 44, Avg. 15 ± 15 Athens: Range 15 - 23, $\sum_{12}$PBDE: 21 - 30	[22]

4.4.2 Aerosol MeO-BDE concentrations

2'-MeO-BDE-68 from 0.0297 - 0.969 pg/m^3 and 6-MeO-BDE-47 were observed from lower than the limit of detection (LOD) to 0.364 pg/m^3 in these collected aerosols. MeO-BDE analytes were found in all 7 MOUDI sample date sets where 6-MeO-BDE-47 was found in 5/7 sample dates and 2'-MeO-BDE-68 was recorded in all sample dates above method detection limits. MeO-BDE were present in 31% of MOUDI sample stages within each sample date set with concentrations between two and ten times lower than anthropogenic PBDE levels. Anthropogenic ∑PBDE levels (Figure 4-1) were 5.1 to 61 times greater than ∑MeO-BDE concentrations for each month of sampling. Choo *et al.*[88] and Kim *et al.*[61] showed a similar relationship in abiotic marine environments, where MeO-BDEs were 55 times and 3 to 63 times lower, respectively, than PBDEs in seawater samples. In contrast to the results in this research, one study measured MeO-BDEs in aerosols in the atmosphere of South Korea, where MeO-BDEs were measured in the atmosphere at greater levels than anthropogenic PBDEs, despite being at lower levels in the local water[61,81]. The only other atmospheric measurements of MeO-BDEs were made by Bidleman *et al.*[19], who measured 2'-MeO-BDE-68 (0.017 ± 0.016 pg/m^3) and 6-MeO-BDE-47 (0.014 ± 0.014 pg/m^3) in gas phase atmospheric samples collected around the Baltic Sea in 2012. However, no MeO-BDEs were detected in aerosols collected in the same study (< 0.004 pg/m^3)[19]. More measurements of MeO-BDE in aerosols are needed to establish trends.

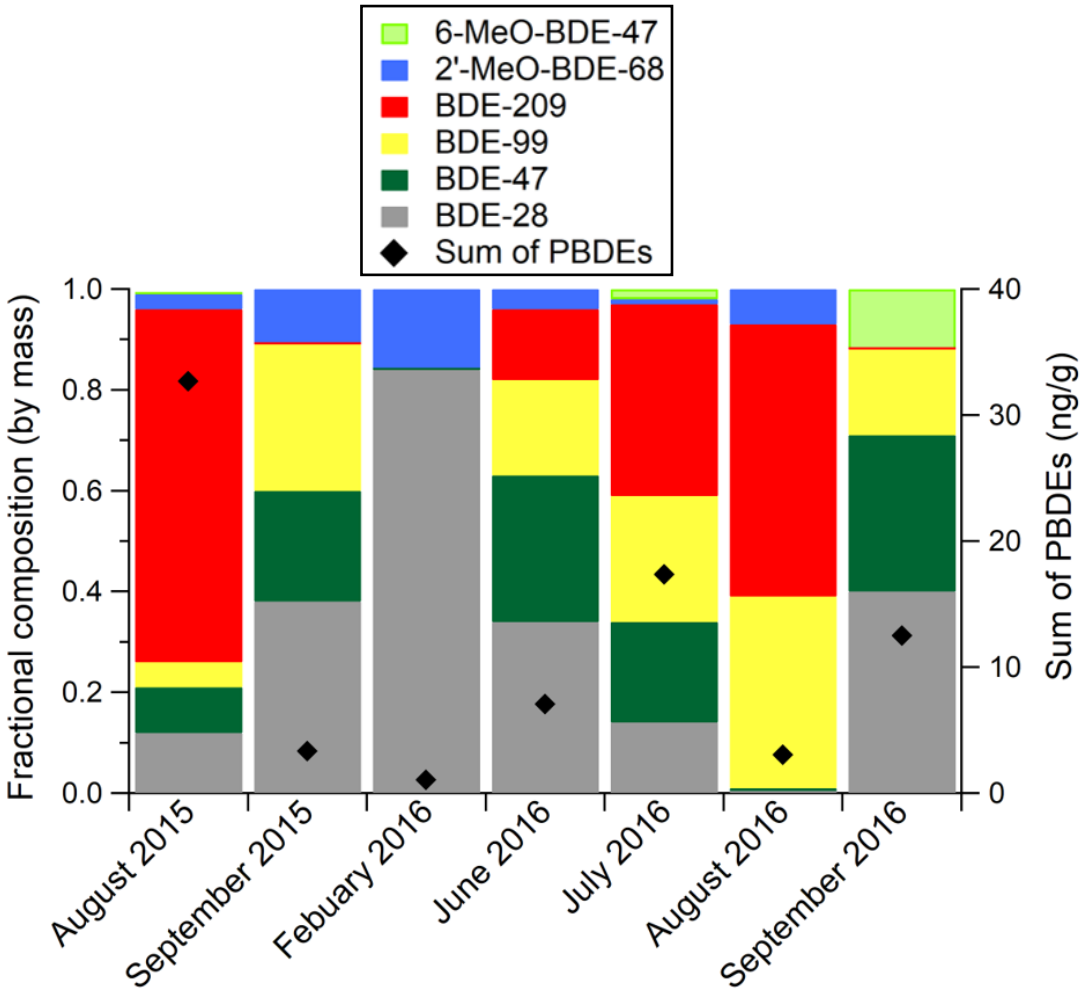

Figure 4-1. Seasonal composition of anthropogenic PBDE and natural MeO-BDE in all MOUDI samples.

4.4.3 Aerosol size distribution of PBDEs

Loadings of PBDEs (sum of BDEs 28, 47, and 99; Figure 4-2) in summer aerosol samples from this study exhibited a trimodal aerosol distribution (ultrafine, fine, and coarse aerosols) among MOUDI sampling size bins. Typical aerosol populations from other atmospheric marine studies have shown a bimodal pattern in total abundance with specific concentration peaks in the fine and coarse mode aerosols that are comparable to aerodynamic size ranges found in this investigation[22,24,25,45,47,89]. However, with this ability

to collect from the nano-aerosol range, the data can be resolved to trimodal patterns. Trimodal PBDE aerosol patterns were also found in aerosol studies taken from urban city and e-waste centre sites[21,47]. Higher levels of PBDEs were measured in the ultrafine aerosol bins (29.23 pg/m^3) during the summer season with respect to the fine aerosol mode (1.70 pg/m^3). The winter season showed similar loadings in the fine mode aerosols (1.05 pg/m^3) and no detectable levels in ultrafine and coarse mode aerosols. In the scenario where PBDE concentrations were underestimated in this study due to blow-off effects (see discussion in Section 4.4.1 above), the trend of increased levels in small aerosols would have been more pronounced[50]. The abundance of these PBDEs in small aerosols may contribute to their LRT.

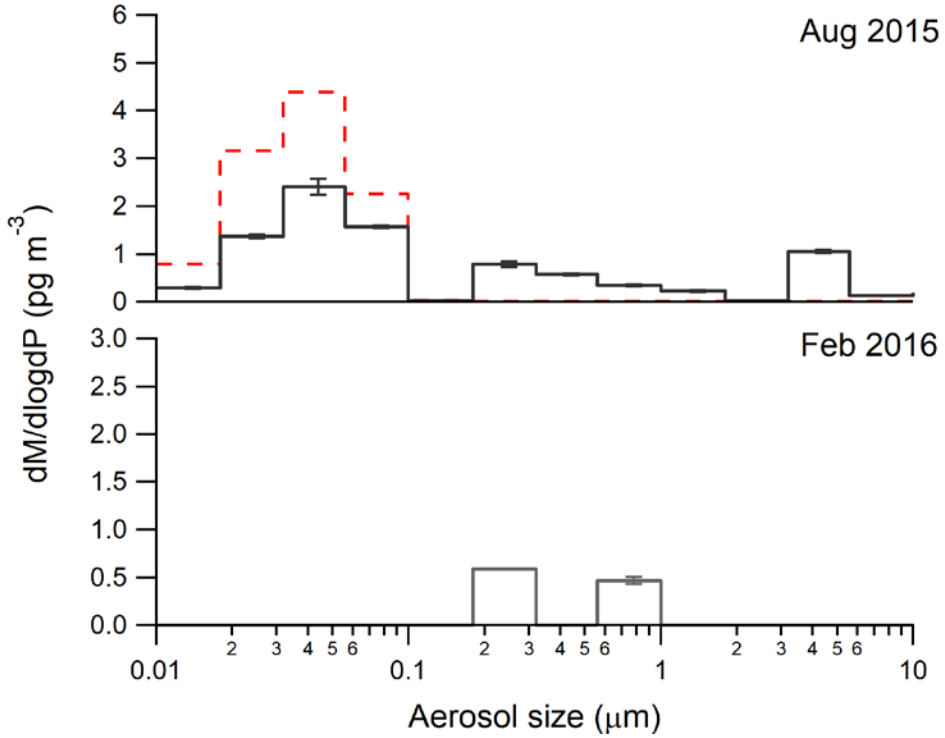

Figure 4-2. Size-resolved aerosol PBDE concentration (sum of BDEs 28, 47, and 99) in Sample 1 (Aug 2015, upper panel) and Sample 3 (Feb 2016, lower panel). Dashed lines

represent the maximum underestimate due to sampling bias[48]. Error bars represent the standard deviation of 3 replicate analyses.

The large PBDE content within summer samples (Figure 4-3) can be attributed primarily to the presence of BDE-209 (23.6 pg/m^3) in the fine aerosol mode. As the largest brominated PBDE congener, BDE-209 possesses the highest K_{oa} constant and lowest vapor pressure among anthropogenic PBDEs making it the most likely to sorb onto aerosols. Fine aerosols become the most receptive to this adsorption process as aerosol surface area trends inversely to aerosol size[41,90]. It is common to see enrichment of organics in these smaller aerosols[21,22,44,46,47].

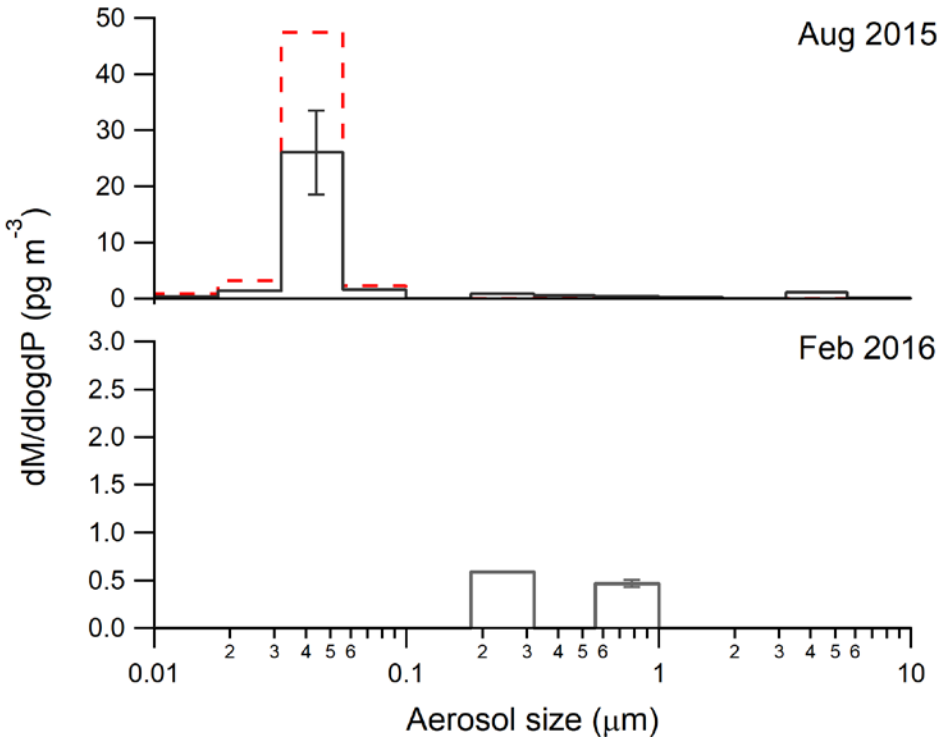

Figure 4-3. Size-resolved aerosol PBDE concentration (BDEs 28, 47, 99, and 209) in Sample 1 (August 2015, upper panel) and Sample 3 (February 2016, lower panel). Dashed lines represent the maximum underestimate due to sampling bias[48]. Error bars represent the standard deviation of 3 replicate analyses.

4.4.4 Aerosol size distribution of MeO-BDEs

Similar to the anthropogenic PBDE results described above, MeO-BDE (6-MeO-BDE-47 and 2'-MeO-BDE-68) aerosol samples (Figure 4-4) showed a trimodal pattern in summer corresponding to characteristic ultrafine, fine, and coarse aerosol size populations and a bimodal pattern in winter with highest levels in ultrafine aerosols.

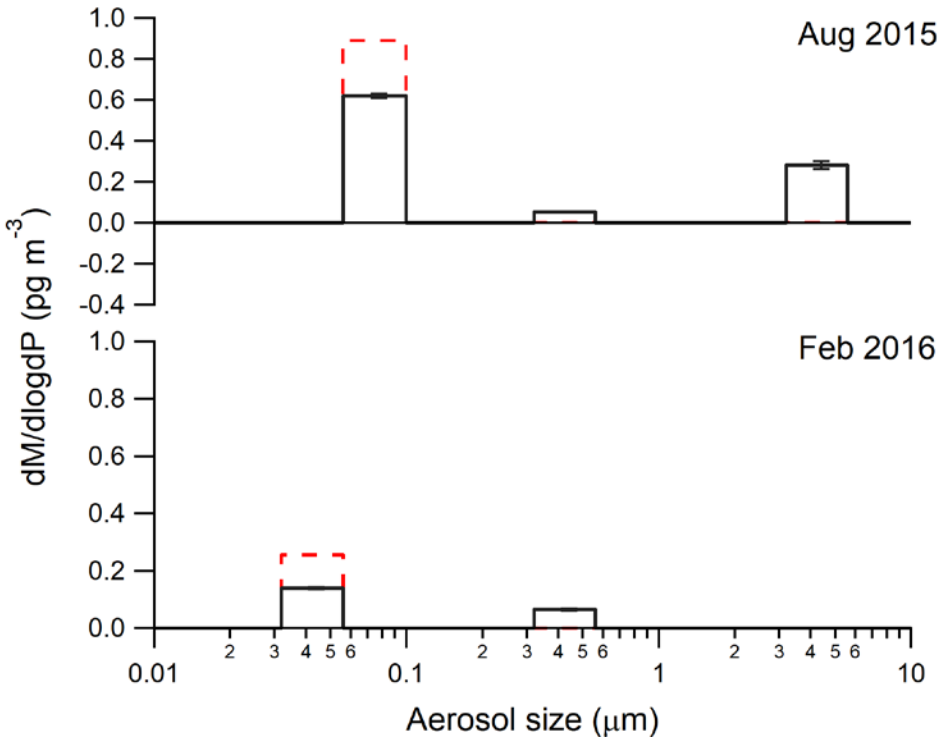

Figure 4-4. Size-resolved 2'-MeO-BDE-68 aerosol concentration in Sample 1 (August 2015, upper panel) and Sample 3 (February 2016, lower panel). Dashed lines represent the maximum underestimate due to sampling bias[48]. Error bars represent the standard deviation of 3 replicate analyses.

4.4.5 Aerosol PBDE temporal trend

Lowest levels of PBDEs (∑PBDE: 1.05 ng/g) and MeO-BDEs (∑MeO-BDE: 0.205 ng/g) were observed in the single winter sample. However, there was variability in abundance through the spring, summer, and fall months. Environmental parameters that could have led to these differences, including $PM_{2.5}$ abundance, temperature, and wind speed were also observed.

Increased $PM_{2.5}$ could cause higher measured aerosol BDEs as an increased condensed phase mass led to enhanced partitioning. No relationship was observed between $PM_{2.5}$ abundance (Figure 4-5) and PBDE aerosol concentrations (R^2 = 0.01, p = 0.817) . Conversely, other studies showed higher PBDE concentrations in the summer than in winter seasons for smaller aerosols (< 0.57 μm diameter)[21–23]. Spring $PM_{2.5}$ aerosols have been shown to be associated with fog and higher PBDE concentrations[44]. Peng *et al.*[91] showed that $PM_{2.5}$ aerosols consisted of high BDE-28, BDE-47, and BDE-99 concentrations during transitional winter/spring than summer/autumn months but were unique to their sampling sites. Conceivable PBDE aerosol sinks during the summer season could come in a form of wet deposition (seasonal rainfall and humidity) that may add mass to $PM_{2.5}$ aerosols, thus shortening their potential to LRT[91]. These results likely vary as a function of local environmental conditions and BDE sources.

Temperature may also play a role in determining BDEs in aerosols. Lower temperature could increase partitioning to aerosols. Measured samples indicated that total aerosol loadings of anthropogenic PBDEs were weakly correlated (R^2 = 0.50, p =

0.076) with the mean ambient temperature. This is in contrast to other studies, which have shown that urban areas had higher aerosol loadings in fine aerosols during the winter; where lower temperatures would lead to more PBDEs absorbing onto fine mode aerosols[21,26,44,92]. Temperature-dependent partitioning cannot explain these observations.

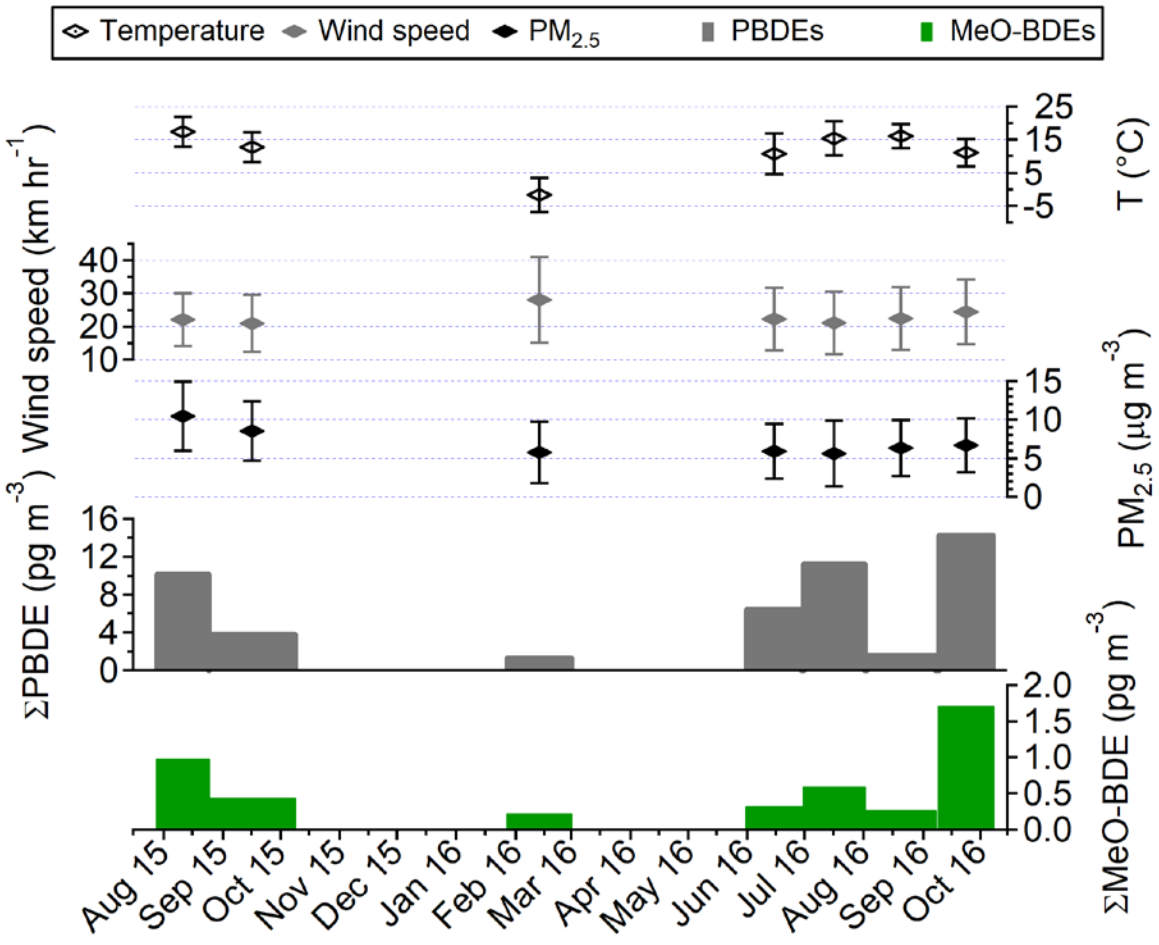

Figure 4-5. PBDE and MeO-BDE concentrations of $PM_{2.5}$ aerosols with respect to their corresponding seasonal environmental parameters (temperature, wind speed).

Wind speed may influence PBDE aerosol loadings. Higher wind speeds lead to higher emission of marine aerosols[93]. If marine aerosols are the source of PBDEs, there

may have been an expected correlation with wind speeds. However, no correlation (R^2 = 0.22, p = 0.288) was observed between BDE loadings and wind speed. Odabasi *et al.*[26] and Bossi *et al.*[68] showed that higher continental wind speeds can lead to higher PBDE levels from the regional resuspension of PBDE-contaminated aerosols. These results were consistent with those of Besis *et al.*[21], who showed that wind speed had no effect on PBDE concentrations but may have been more influenced by local emissions. In this case, wind speed may not account for PBDE levels in the MOUDI aerosol samples.

Considering that seasonal temperature, wind speed, and $PM_{2.5}$ abundance may not be able to explain the observed temporal trends of PBDEs in aerosols, PBDE sources could be potentially derived from local indoor-outdoor exchanges or could be a product of LRT from ocean productivity. Primarily, anthropogenic PBDEs may come from indoor gas emissions produced by household and office workspace ventilation[48]. PBDE sources may also originate indirectly via analyte deposition (gas phase condensation) onto dust. It is known that BDE-209 is found in house dust that are likely caused by the abrasion of consumer products[48,94]. Increased loadings of these larger PBDEs during the warm season in this study, detectable BDE-209 loadings (1.03 - 23.6 pg/m^3), may indicate the possibility that indoor sources contribute to PBDE loadings before being degraded into smaller PBDE congeners. Conversely, long range sources (Figure 4-6) may show other origins by illustrating back trajectories of aerosols collected by the MOUDI setup that have traveled into NL from mainland Canada (Figure 4-6A) in the warm season and from the Atlantic Ocean (Figure 4-6B) in the cold season. It is known that Arctic environments are

susceptible to POP exposure through the rapid and efficient LRT within the atmosphere[95,96].

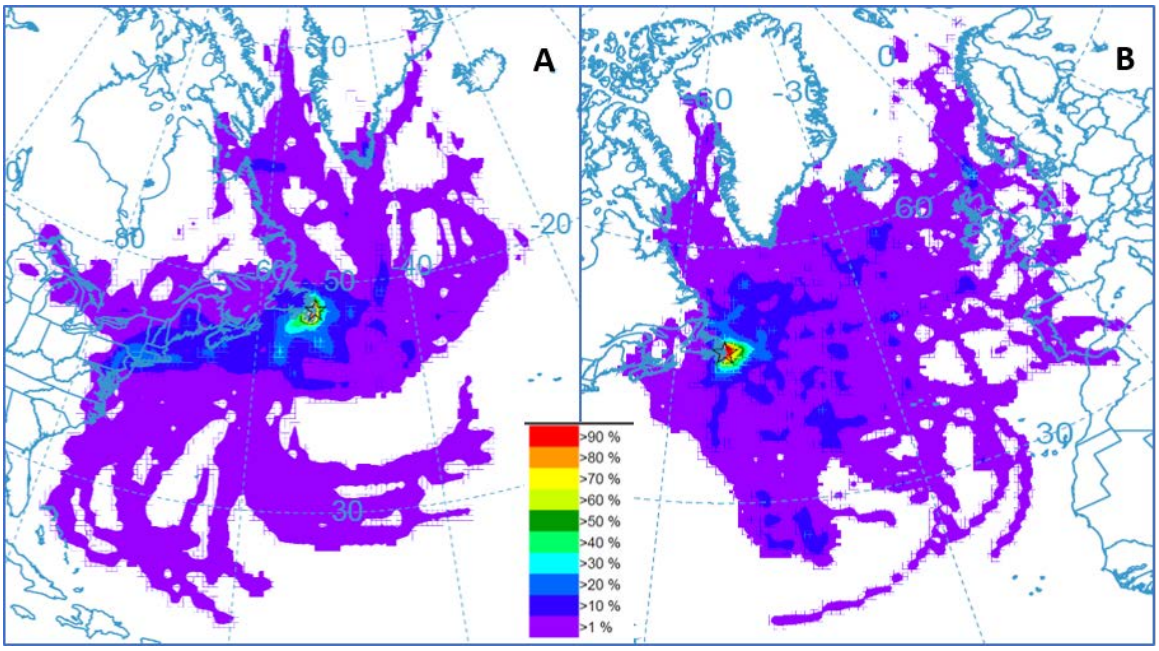

Figure 4-6. Hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model wind back trajectories (A) Sample 2, August 2015 (B) Sample 3, February 2016.

4.4.6 Aerosol MeO-BDE temporal trend

Total MeO-BDE concentrations were higher during the summer season (0.235 - 0.969 pg/m^3) compared to colder winter temperatures (0.205 pg/m^3, Figure 4-5). No significant correlations were observed between MeO-BDE aerosol loadings and wind velocity (R^2 = 0.27, p = 0.232), temperature (R^2 = 0.14, p = 0.409) or $PM_{2.5}$ (R^2 = 0.20, p = 0.447). This suggests that marine aerosol emission is not the dominant factor in determining MeO-BDE aerosol loadings. However, emissions of MeO-BDEs into marine aerosols may not be consistent through the year. Summer growth of organisms that produce natural MeO-BDE analogues, such as blue mussels and phytoplankton production, is expected. Lofstrand *et al.*[17] conducted a seasonal study that discovered

precursors to MeO-BDE (bromophenols) and MeO-BDEs in summer algae. As a result, wind velocity may not act as a good proxy for marine aerosol contribution.

4.5 Conclusions

PBDE and MeO-BDE aerosol loadings were shown to be mostly associated with fine and ultrafine aerosol modes. The winter seasons showed a bimodal collection in the fine and ultrafine aerosol modes that would lead to a greater LRT. Seasonal environmental parameters (i.e. wind and temperature) may affect long range travel through these small aerosols. There was no correlation of aerosol PBDE or MeO-BDE concentration with wind velocity or $PM_{2.5}$ aerosol abundance. However, seasonal temperatures had a moderate correlation to PBDEs found in atmospheric samples. This contrasts with previous studies that showed increases in winter caused by temperature-dependent partitioning to aerosols. Increased aerosol PBDEs in summer could be caused by local indoor-outdoor exchange or from changes in air mass sources. Anthropogenic PBDE concentrations were greater than MeO-BDE throughout the year and experienced similar aerosol collection patterns seasonally. Increased natural MeO-BDEs in summer may be associated with increased ocean phytoplanktonic production. Future work with the same limitations encountered during this campaign may consist of more MOUDI sampling that would include additional colder season collections.

4.6 References

(1) Wiseman, S. B.; Wan, Y.; Chang, H.; Zhang, X.; Hecker, M.; Jones, P. D.; Giesy, J. P. Polybrominated Diphenyl Ethers and Their Hydroxylated/Methoxylated Analogs: Environmental Sources, Metabolic Relationships, and Relative Toxicities. *6th Int. Conf. Mar. Pollut. Ecotoxicol.* **2011**, *63* (5–12), 179–188. https://doi.org/http://dx.doi.org/10.1016/j.marpolbul.2011.02.008.

(2) Dishaw, L. V; Macaulay, L. J.; Roberts, S. C.; Stapleton, H. M. Exposures, Mechanisms, and Impacts of Endocrine-Active Flame Retardants. *Curr. Opin. Pharmacol.* **2014**, *19* (117), 125–133. https://doi.org/10.1016/j.coph.2014.09.018.

(3) Noyes, P. D.; Lema, S. C.; Macaulay, L. J.; Douglas, N. K.; Stapleton, H. M. Low Level Exposure to the Flame Retardant BDE-209 Reduces Thyroid Hormone Levels and Disrupts Thyroid Signaling in Fathead Minnows. *Environ. Sci. Technol.* **2013**, *47* (17), 10012–10021.

(4) Noyes, P. D.; Hinton, D. E.; Stapleton, H. M. Accumulation and Debromination of Decabromodiphenyl Ether (BDE-209) in Juvenile Fathead Minnows (Pimephales Promelas) Induces Thyroid Disruption and Liver Alterations. *Toxicol. Sci.* **2011**, *122* (2), 265–274. https://doi.org/10.1093/toxsci/kfr105; 10.1093/toxsci/kfr105.

(5) Secretariat of the Stockholm Convention on Persistent Organic Pollutants United Nations Environment Programme (UNEP) Chemicals International Environment House. *Ridding the World of POPs: A Guide to the Stockholm Convention*; United Nations Environment Programme: Châtelaine, Geneva, Switzerland, 2005.

(6) Hassan, Y.; Shoeib, T. Levels of Polybrominated Diphenyl Ethers and Novel Flame Retardants in Microenvironment Dust from Egypt: An Assessment of Human Exposure. *Sci. Total Environ.* **2015**, *505*, 47–55. https://doi.org/http://dx.doi.org/10.1016/j.scitotenv.2014.09.080.

(7) Chen, D.; Hale, R. C.; Letcher, R. J. Photochemical and Microbial Transformation of Emerging Flame Retardants: Cause for Concern? *Environ. Toxicol. Chem.* **2015**, *34* (4), 687–699. https://doi.org/10.1002/etc.2858.

(8) Vorkamp, K.; Riget, F. F.; Bossi, R.; Dietz, R. Temporal Trends of Hexabromocyclododecane, Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Ringed Seals from East Greenland. *Environ. Sci. Technol.* **2011**, *45* (4), 1243–1249. https://doi.org/10.1021/es102755x.

(9) Vetter, W.; Stoll, E.; Garson, M. J.; Fahey, S. J.; Gaus, C.; Müller, J. F. Sponge Halogenated Natural Products Found at Parts-per-million Levels in Marine Mammals. *Environ. Toxicol. Chem.* **2002**, *21* (10), 2007–2259.

(10) Malmvärn, A.; Marsh, G.; Kautsky, L.; Athanasiadou, M.; Bergman, Å.; Asplund, L. Hydroxylated and Methoxylated Brominated Diphenyl Ethers in the Red Algae Ceramium Tenuicorne and Blue Mussels from the Baltic Sea. *Environ. Sci. Technol.* **2005**, *39* (9), 2990–2997. https://doi.org/10.1021/es0482886.

(11) Bidleman, T. F.; Agosta, K.; Andersson, A.; Haglund, P.; Nygren, O.; Ripszam, M.; Tysklind, M. Air-Water Exchange of Brominated Anisoles in the Northern Baltic Sea. *Environ. Sci. Technol.* **2014**, *48* (11), 6124–6132. https://doi.org/10.1021/es5007109.

(12) Schorn, M. A.; Jordan, P. A.; Podell, S.; Blanton, J. M.; Agarwal, V.; Biggs, J. S.; Allen, E. E.; Moorea, B. S. Comparative Genomics of Cyanobacterial Symbionts Reveals Distinct, Specialized Metabolism in Tropical Dysideidae Sponges. *Am. Soc. Microbiol.* **2019**, *10* (3), 1–15.

(13) Teuten, E. L.; Xu, L.; Reddy, C. M. Two Abundant Bioaccumulated Halogenated Compounds Are Natural Products. *Science* **2005**, *307*, 917–920. https://doi.org/10.1126/science.1106882.

(14) Qiu, X.; Mercado-Feliciano, M.; Bigsby, R. M.; Hites, R. A. Measurement of Polybrominated Diphenyl Ethers and Metabolites in Mouse Plasma after Exposure to a Commercial Pentabromodiphenyl Ether Mixture. *Environ. Health Perspect.* **2007**, *115* (7), 1052–1058. https://doi.org/10.1289/ehp.10011.

(15) Malmvärn, A.; Zebühr, Y.; Kautsky, L.; Bergman, Å.˚; Asplund, L. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers and Polybrominated Dibenzo-p-Dioxins in Red Alga and Cyanobacteria Living in the Baltic Sea. *Chemosphere* **2008**, *72* (6), 910–916. https://doi.org/10.1016/j.chemosphere.2008.03.036.

(16) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated Flame Retardants in the Arctic Environment - Trends and New Candidates. *Sci. Total Environ.* **2010**, *408* (15), 2885–2918. https://doi.org/10.1016/j.scitotenv.2009.08.037.

(17) Löfstrand, K.; Liu, X.; Lindqvist, D.; Jensen, S.; Asplund, L. Seasonal Variations of Hydroxylated and Methoxylated Brominated Diphenyl Ethers in Blue Mussels from the Baltic Sea. *Chemosphere* **2011**, *84* (4), 527–532. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2011.01.001.

(18) Erratico, C. A.; Szeitz, A.; Bandiera, S. M. Oxidative Metabolism of BDE-99 by Human Liver Microsomes: Predominant Role of CYP2B6. *Toxicol. Sci.* **2012**, *129* (2), 280–292. https://doi.org/10.1093/toxsci/kfs215.

(19) Bidleman, T. F.; Agosta, K.; Andersson, A.; Haglund, P.; Liljelind, P.; Hegmans, A.; Jantunen, L. M.; Nygren, O.; Poole, J.; Ripszam, M.; et al. Sea-Air Exchange of Bromoanisoles and Methoxylated Bromodiphenyl Ethers in the Northern Baltic. *Mar. Pollut. Bull.* **2016**, *112* (1–2), 58–64. https://doi.org/10.1016/j.marpolbul.2016.08.042.

(20) Bidleman, T. F.; Brorström-Lundén, E.; Hansson, K.; Laudon, H.; Nygren, O.; Tysklind, M. Atmospheric Transport and Deposition of Bromoanisoles Along a Temperate to Arctic Gradient. *Environ. Sci. Technol.* **2017**, *51* (19), 10974–10982. https://doi.org/10.1021/acs.est.7b03218.

(21) Besis, A.; Botsaropoulou, E.; Voutsa, D.; Samara, C. Particle-Size Distribution of Polybrominated Diphenyl Ethers (PBDEs) in the Urban Agglomeration of Thessaloniki, Northern Greece. *Atmos. Environ.* **2015**, *104*, 176–185. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2015.01.019.

(22) Mandalakis, M.; Besis, A.; Stephanou, E. G. Particle-Size Distribution and Gas/Particle Partitioning of Atmospheric Polybrominated Diphenyl Ethers in Urban Areas of Greece. *Environ. Pollut.* **2009**, *157* (4), 1227–1233. https://doi.org/10.1016/j.envpol.2008.12.010.

(23) Dall'Osto, M.; Beddows, D. C. S.; Tunved, P.; Harrison, R. M.; Lupi, A.; Vitale, V.; Becagli, S.; Traversi, R.; Park, K.-T.; Yoon, Y. J.; et al. Apportioning Aerosol Natural and Anthropogenic Sources Thorough Simultaneous Aerosol Size Distributions and Chemical Composition in the European High Arctic. *Atmos. Chem. Phys. Discuss.* **2018**, 1–46. https://doi.org/10.5194/acp-2018-447.

(24) Okonski, K.; Degrendele, C.; Melymuk, L.; Landlová, L.; Kukučka, P.; Vojta, Š.; Kohoutek, J.; Cupr, P.; Klánová, J. Particle Size Distribution of Halogenated Flame Retardants and Implications for Atmospheric Deposition and Transport. *Environ. Sci. Technol.* **2014**, *48* (24), 14426−14434.

(25) O'Dowd, C. D.; Facchini, M. C.; Cavalli, F.; Ceburnis, D.; Mircea, M.; Decesari, S.; Fuzzi, S.; Yoon, Y. J.; Putaud, J.-P. Biogenically Driven Organic Contribution to Marine Aerosol. *Nature* **2004**, *431* (7009), 676–680. https://doi.org/10.1038/nature02959.

(26) Odabasi, M.; Cetin, B.; Bayram, A. Persistent Organic Pollutants (POPs) on Fine and Coarse Atmospheric Particles Measured at Two (Urban and Industrial) Sites. *Aerosol Air Qual. Res.* **2015**, *15* (5), 1894–1905. https://doi.org/10.4209/aaqr.2015.02.0118.

(27) Wang, C.; Li, W.; Chen, J.; Wang, H.; Li, T.; Shen, G.; Shen, H.; Huang, Y.; Wang, R.; Wang, B.; et al. Summer Atmospheric Polybrominated Diphenyl Ethers in Urban and Rural Areas of Northern China. *Environ. Pollut.* **2012**, *171*, 234–240. https://doi.org/10.1016/j.envpol.2012.07.041.

(28) Chen, M.; Jiang, J.; Gan, Z.; Yan, Y.; Ding, S.; Su, S.; Bao, X. Grain Size Distribution and Exposure Evaluation of Organophosphorus and Brominated Flame Retardants in Indoor and Outdoor Dust and PM10 from Chengdu, China. *J. Hazard. Mater.* **2018**, *365*, 280–288. https://doi.org/10.1016/j.jhazmat.2018.10.082.

(29) de la Torre, A.; Barbas, B.; Sanz, P.; Navarro, I.; Artíñano, B.; Martínez, M. A. Traditional and Novel Halogenated Flame Retardants in Urban Ambient Air: Gas-Particle Partitioning, Size Distribution and Health Implications. *Sci. Total Environ.* **2018**, *630* (40), 154–163. https://doi.org/10.1016/j.scitotenv.2018.02.199.

(30) Degrendele, C.; Wilson, J.; Kukučka, P.; Klánová, J.; Lammel, G. Are Atmospheric PBDE Levels Declining in Central Europe ? Examination of the Seasonal Variations , Gas-Particle Partitioning and Implications for Long-Range Atmospheric Transport. **2018**, *18* (17), 12877–12890.

(31) Zhang, X. Particle Size Distributions of PCDD/Fs and PBDD/Fs in Ambient Air in a Suburban Area in Beijing, China. *Aerosol Air Qual. Res.* **2015**, *15*, 1933–1943. https://doi.org/10.4209/aaqr.2015.06.0421.

(32) Dong, Y.; Fu, S.; Zhang, Y.; Nie, H.; Li, Z. Polybrominated Diphenyl Ethers in Atmosphere from Three Different Typical Industrial Areas in Beijing, China. *Chemosphere* **2015**, *123*, 33–42. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2014.11.043.

(33) Egebäck, A. L.; Sellström, U.; McLachlan, M. S. Decabromodiphenyl Ethane and Decabromodiphenyl Ether in Swedish Background Air. *Chemosphere* **2012**, *86* (3), 264–269. https://doi.org/10.1016/j.chemosphere.2011.09.041.

(34) Kurt-Karakus, P. B.; Alegria, H.; Jantunen, L.; Birgul, A.; Topcu, A.; Jones, K. C.; Turgut, C. Polybrominated Diphenyl Ethers (PBDEs) and Alternative Flame Retardants (NFRs) in Indoor and Outdoor Air and Indoor Dust from Istanbul-Turkey: Levels and an Assessment of Human Exposure. *Atmos. Pollut. Res.* **2017**, *8* (5), 801–815. https://doi.org/10.1016/j.apr.2017.01.010.

(35) Deng, W. J.; Zheng, J. S.; Bi, X. H.; Fu, J. M.; Wong, M. H. Distribution of PBDEs in Air Particles from an Electronic Waste Recycling Site Compared with Guangzhou and Hong Kong, South China. *Environ. Int.* **2007**, *33* (8), 1063–1069. https://doi.org/10.1016/j.envint.2007.06.007.

(36) Xiao, H.; Hung, H.; Wania, F.; Lao, R.; Sabljic, E.; Sverko, E.; Lei, Y. D.; Fellin, P.; Barresi, E. Field Evaluation of a Flow-through Sampler for Measuring Pesticides and Brominated Flame Retardants in the Arctic Atmosphere. *Environ. Sci. Technol.* **2012**, *46* (14), 7669–7676. https://doi.org/10.1021/es301481w.

(37) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820–1826. https://doi.org/10.1021/es103803t.

(38) Besis, A.; Voutsa, D.; Samara, C. Atmospheric Occurrence and Gas-Particle Partitioning of PBDEs at Industrial, Urban and Suburban Sites of Thessaloniki, Northern Greece: Implications for Human Health. *Environ. Pollut.* **2016**, *215*, 113–124. https://doi.org/10.1016/j.envpol.2016.04.093.

(39) Mulder, M. D.; Heil, A.; Kukučka, P.; Kuta, J.; Přibylová, P.; Prokeš, R.; Lammel, G. Long-Range Atmospheric Transport of PAHs, PCBs and PBDEs to the Central and Eastern Mediterranean and Changes of PCB and PBDE Congener Patterns in Summer 2010. *Atmos. Environ.* **2015**, *111* (0), 51–59. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2015.03.044.

(40) Li, Y.; Lin, T.; Wang, F.; Ji, T.; Guo, Z. Seasonal Variation of Polybrominated Diphenyl Ethers in PM2.5 Aerosols over the East China Sea. *Chemosphere* **2015**, *119*, 675–681. https://doi.org/10.1016/j.chemosphere.2014.07.083.

(41) Besis, A.; Lammel, G.; Kukučka, P.; Samara, C.; Sofuoglu, A.; Dumanoglu, Y.; Eleftheriadis, K.; Kouvarakis, G.; Sofuoglu, S. C.; Vassilatou, V.; et al. Polybrominated Diphenyl Ethers (PBDEs) in Background Air around the Aegean: Implications for Phase Partitioning and Size Distribution. *Environ. Sci. Pollut. Res.* **2017**, *24* (36), 28102–28120. https://doi.org/10.1007/s11356-017-0285-7.

(42) Zhu, Y.-S.; Yang, W.-D.; Li, X.-W.; Ni, H.-G.; Zeng, H. Airborne Particle-Bound Brominated Flame Retardants: Levels, Size Distribution and Indoor-Outdoor Exchange. *Environ. Pollut.* **2017**, *233*, 1104–1112. https://doi.org/10.1016/j.envpol.2017.10.013.

(43) Cao, Z.; Zhao, L.; Meng, X.; Liu, X.; Wu, P.; Fan, X.; Wang, S.; Jie, J.; Miao, Z.; Xu, X.; et al. Amplification Effect of Haze on Human Exposure to Halogenated Flame Retardants in Atmospheric Particulate Matter and the Corresponding Mechanism. *J. Hazard. Mater.* **2018**, *359*, 491–499. https://doi.org/10.1016/j.jhazmat.2018.07.109.

(44) Lyu, Y.; Xu, T.; Li, X.; Cheng, T.; Yang, X.; Sun, X.; Chen, J. Particle-Size Distribution of Polybrominated Diphenyl Ethers (PBDEs) and Its Implications for Health. *Atmos. Meas. Tech. Discuss.* **2015**, *8* (12), 12955–12992. https://doi.org/10.5194/amtd-8-12955-2015.

(45) Cao, R.; Zhang, H.; Zhao, L.; Zhang, Y.; Geng, N.; Teng, M.; Zou, L.; Gao, Y.; Ni, Y.; Fu, Q.; et al. Hazy Weather-Induced Variation in Environmental Behavior of PCDD/Fs and PBDEs in Winter Atmosphere of A North China Megacity. *Environ. Sci. Technol.* **2018**, *52* (15), 8173–8182. https://doi.org/10.1021/acs.est.8b02148.

(46) Zhang, B.-Z.; Zhang, K.; Li, S.-M.; Wong, C. S.; Zeng, E. Y. Size-Dependent Dry Deposition of Airborne Polybrominated Diphenyl Ethers in Urban Guangzhou, China. *Environ. Sci. Technol.* **2012**, *46* (13), 7207–7214.

(47) Luo, P.; Ni, H.-G.; Bao, L.-J.; Li, S.-M.; Zeng, E. Y. Size Distribution of Airborne Particle-Bound Polybrominated Diphenyl Ethers and Its Implications for Dry and Wet Deposition. *Environ. Sci. Technol.* **2014**, *48* (23), 13793–13799.

(48) Richman, K. E.; Butt, C. M.; Young, C. J. Supplemental: Size-Resolved Particle Measurements of Polybrominated Diphenyl Ethers Indoors: Implications for Sources and Human Exposure. *Environ. Toxicol. Chem.* **2018**, *37* (2), 481–490. https://doi.org/10.1002/etc.3981.

(49) Wang, X.; Deane, G. B.; Moore, K. A.; Ryder, O. S.; Stokes, M. D.; Beall, C. M.; Collins, D. B.; Santander, M. V.; Burrows, S. M.; Sultana, C. M.; et al. The Role of Jet and Film Drops in Controlling the Mixing State of Submicron Sea Spray Aerosol Particles. *Proc. Natl. Acad. Sci.* **2017**, *114* (27), 6978–6983. https://doi.org/10.1073/pnas.1702420114.

(50) Richman, K. E.; Butt, C. M.; Young, C. J. Size-Resolved Particle Measurements of Polybrominated Diphenyl Ethers Indoors: Implications for Sources and Human Exposure. *Environ. Toxicol. Chem.* **2018**, *37* (2), 481–490. https://doi.org/10.1002/etc.3981.

(51) Li, T.; Zhou, J.; Wu, C.; Bao, L.; Shi, L.; Zeng, E. Y. Characteristics of Polybrominated Diphenyl Ethers Released from Thermal Treatment and Open Burning of E-Waste Characteristics of Polybrominated Diphenyl Ethers Released from Thermal Treatment and Open Burning of E-Waste. **2018**, *52* (8), 4650–4657. https://doi.org/10.1021/acs.est.8b00780.

(52) Yu, Y.; Hung, H.; Alexandrou, N.; Roach, P.; Nordin, K. Multiyear Measurements of Flame Retardants and Organochlorine Pesticides in Air in Canada's Western Sub-Arctic. *Environ. Sci. Technol.* **2015**, *49* (14), 8623–8630. https://doi.org/10.1021/acs.est.5b01996.

(53) Wang, P.; Li, Y.; Zhang, Q.; Yang, Q.; Zhang, L.; Liu, F.; Fu, J.; Meng, W.; Wang, D.; Sun, H.; et al. Three-Year Monitoring of Atmospheric PCBs and PBDEs at the Chinese Great Wall Station, West Antarctica: Levels, Chiral Signature, Environmental Behaviors and Source Implication. *Atmos. Environ.* **2017**, *150*, 407–416. https://doi.org/10.1016/j.atmosenv.2016.11.036.

(54) Bossi, R.; Vorkamp, K.; Skov, H. Concentrations of Organochlorine Pesticides, Polybrominated Diphenyl Ethers and Perfluorinated Compounds in the Atmosphere of North Greenland. *Environ. Pollut.* **2016**, *217*, 4–10. https://doi.org/10.1016/j.envpol.2015.12.026.

(55) Davie-Martin, C.; Hageman, K.; Chin, Y.-P.; Nistor, B.; Hung, H. Concentrations, Gas-Particle Distributions, and Source Indicator Analysis of Brominated Flame Retardants in Air at Toolik Lake, Arctic Alaska. *Environ. Sci. Process. Impacts* **2016**, *18*, 1274–1284. https://doi.org/10.1039/C6EM00395H.

(56) Salamova, A.; Hermanson, M. H.; Hites, R. A. Organophosphate and Halogenated Flame Retardants in Atmospheric Particles from a European Arctic Site. *Environ. Sci. Technol.* **2014**, *48* (11), 6133–6140.

(57) McDonough, C. A.; Puggioni, G.; Helm, P. A.; Muir, D. C. G.; Lohmann, R. Spatial Distribution and Air-Water Exchange of Organic Flame Retardants in the Lower Great Lakes. *Environ. Sci. Technol.* **2016**, *50* (17), 9133–9141. https://doi.org/10.1021/acs.est.6b02496.

(58) Möller, A.; Xie, Z.; Cai, M.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants and Dechlorane plus in the Marine Atmosphere from Southeast Asia toward Antarctica. *Environ. Sci. Technol.* **2012**, *46* (6), 3141–3148. https://doi.org/10.1021/es300138q.

(59) Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. Occurrence and Air-Seawater Exchange of Brominated Flame Retardants and Dechlorane Plus in the North Sea. *Atmos. Environ.* **2012**, *46*, 346–353. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2011.09.055.

(60) Möller, A.; Xie, Z.; Cai, M. M.; Zhong, G.; Huang, P.; Cai, M. M.; Sturm, R.; He, J.; Ebinghaus, R. Polybrominated Diphenyl Ethers vs Alternate Brominated Flame Retardants and Dechloranes from East Asia to the Arctic. *Environ. Sci. Technol.* **2011**, *45* (16), 6793–6799. https://doi.org/10.1021/es201850n.

(61) Kim, U.-J. J.; Yen, N. T. H.; Oh, J.-E. E. Correction to Hydroxylated, Methoxylated, and Parent Polybrominated Diphenyl Ethers (PBDEs) in the Inland Environment, Korea and Potential OH- and MeO-BDE Source. *Environ. Sci. Technol.* **2014**, *48* (13), 7245–7253. https://doi.org/10.1021/es5006972.

(62) Li, Y.; Geng, D.; Liu, F.; Wang, T.; Wang, P.; Zhang, Q.; Jiang, G. Study of PCBs and PBDEs in King George Island, Antarctica, Using PUF Passive Air Sampling. *Atmos. Environ.* **2012**, *51*, 140–145. https://doi.org/10.1016/j.atmosenv.2012.01.034.

(63) Khairy, M. A.; Luek, J.; Dickhut, R. M.; Lohmann, R. Levels, Sources, and Chemical Fate of Persistent Organic Pollutants in the Atmosphere and Snow along the Western Antarctic Peninsula. *Rev.* **2016**, *216*, 304–313. https://doi.org/10.1016/j.envpol.2016.05.092.

(64) Lohmann, R.; Klánová, J.; Kukučka, P.; Yonis, S.; Bollinger, K. Concentrations, Fluxes, and Residence Time of PBDEs across the Tropical Atlantic Ocean. *Environ. Sci. Technol.* **2013**, *47* (24), 13967–13975. https://doi.org/10.1021/es403494b.

(65) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polybrominated Diphenyl Ethers (PBDEs) and Alternative Brominated Flame Retardants in Air and Seawater of the European Arctic. *Environ. Pollut.* **2011**, *159* (6), 1577–1583. https://doi.org/10.1016/j.envpol.2011.02.054.

(66) Li, J.; Li, Q.; Gioia, R.; Zhang, Y.; Zhang, G.; Li, X.; Spiro, B.; Bhatia, R. S.; Jones, K. C. PBDEs in the Atmosphere over the Asian Marginal Seas, and the Indian and Atlantic Oceans. *Atmos. Environ.* **2011**, *45* (37), 6622–6628. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2011.09.010.

(67) Venier, M.; Ma, Y.; Hites, R. A. Brominated Flame Retardants in the Great Lakes Atmosphere. *Environ. Sci. Technol.* **2012**, *46* (13), 8653–8660. https://doi.org/dx.doi.org/10.1021/es3015919.

(68) Bossi, R.; Skov, H.; Vorkamp, K.; Christensen, J.; Rastogi, S. C.; Egeløv, A.; Petersen, D. Atmospheric Concentrations of Organochlorine Pesticides, Polybrominated Diphenyl Ethers and Polychloronaphthalenes in Nuuk, South-West Greenland. *Atmos. Environ.* **2008**, *42* (31), 7293–7303. https://doi.org/10.1016/j.atmosenv.2008.06.049.

(69) Su, Y.; Hung, H.; Sverko, E.; Fellin, P.; Li, H. Multi-Year Measurements of Polybrominated Diphenyl Ethers (PBDEs) in the Arctic Atmosphere. *Atmos. Environ.* **2007**, *41* (38), 8725–8735. https://doi.org/10.1016/j.atmosenv.2007.07.032.

(70) Wang, X. M.; Ding, X.; Mai, B. X.; Xie, Z. Q.; Xiang, C. H.; Sun, L. G.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Polybrominated Diphenyl Ethers in Airborne Particulates Collected during a Research Expedition from the Bohai Sea to the Arctic. *Environ. Sci. Technol.* **2005**, *39* (20), 7803–7809. https://doi.org/10.1021/es051088p.

(71) Lee, R. G. M.; Thomas, G. O.; Jones, K. C. PBDEs in the Atmosphere of Three Locations in Western Europe. *Environ. Sci. Technol.* **2004**, *38* (3), 699–706. https://doi.org/10.1021/es035042c.

(72) Weather for Your World https://customweather.com/.

(73) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) https://ready.arl.noaa.gov/HYSPLIT.php.

(74) Stein, A.F., Draxler, R.R, Rolph, G.D., Stunder, B.J.B., Cohen, M.D., and Ngan, F.; Stein, A. F.; Draxler, R. R.; Rolph, G. D.; Stunder, B. J. B.; Cohen, M. D.; Ngan, F. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bull. Amer. Meteor. Soc.* **2015**, *96* (96), 2059–2077. https://doi.org/10.1175/BAMS-D-14-00220.1.

(75) Rolph, G. D. Real-time Environmental Applications and Display sYstem (READY) http://ready.arl.noaa.gov.

(76) Gouin, T.; Thomas, G. O.; Chaemfa, C.; Harner, T.; Mackay, D.; Jones, K. C. Concentrations of Decabromodiphenyl Ether in Air from Southern Ontario: Implications for Particle-Bound Transport. *Chemosphere* **2006**, *64* (2), 256–261. https://doi.org/10.1016/j.chemosphere.2005.12.071.

(77) Li, Y.-F.; Qiao, L.-N.; Ren, N.-Q.; Sverko, E.; Mackay, D.; Macdonald, R. W. Decabrominated Diphenyl Ethers (BDE-209) in Chinese and Global Air: Levels, Gas/Particle Partitioning, and Long-Range Transport: Is Long-Range Transport of BDE-209 Really Governed by the Movement of Particles? *Environ. Sci. Technol.* **2017**, *51* (2), 1035–1042. https://doi.org/10.1021/acs.est.6b05395.

(78) Watanabe, I.; Sakai, S. Environmental Release and Behavior of Brominated Flame Retardants. *Environ. Int.* **2003**, *29* (6), 665–682. https://doi.org/10.1016/s0160-4120(03)00123-5.

(79) Nguyen Thanh Dien, N. T.; Yasuhiro Hirai, Y.; Shin-ichi Sakai, S. -i. Correlation between Atmospheric Boundary Layer Height and Polybrominated Diphenyl Ether Concentrations in Air. *Environ. Sci. Technol.* **2017**, *51* (1), 356–364. https://doi.org/10.1021/acs.est.6b03004.

(80) Zhu, Y.-J.; Sun, D.; Yang, N.-E.; Ding, Y.-S.; Feng, W.-B.; Hong, W.-J.; Zhu, S.-M.; Li, Y.-F. Temporal and Spatial Distributions of PBDEs in Atmosphere at Shanghai Rural Regions, China. *Environ. Sci. Pollut. Res.* **2017**, *24* (11), 10885–10892. https://doi.org/10.1007/s11356-017-8646-9.

(81) Kim, U. J.; Yen, N. T. H.; Oh, J. E. Hydroxylated, Methoxylated, and Parent Polybrominated Diphenyl Ethers (PBDEs) in the Inland Environment, Korea, and Potential OH- and MeO-BDE Source. *Environ. Sci. Technol.* **2014**, *48* (13), 7245–7253. https://doi.org/10.1021/es5006972.

(82) Melymuk, L.; Bohlin-Nizzetto, P.; Prokeš, R.; Kukučka, P.; Klánová, J. Sampling Artifacts in Active Air Sampling of Semivolatile Organic Contaminants: Comparing Theoretical and Measured Artifacts and Evaluating Implications for Monitoring Networks. *Environ. Pollut.* **2016**, *217*, 97–106. https://doi.org/10.1016/j.envpol.2015.12.015.

(83) Van Vaeck. L.; Van Cauwenberghe, K. . J. J. The Gas-Particle Distribution of Organic Aerosol Constituents: Measurement of the Volatilisation Artefact in Hi-Vol Cascade Impactor Sampling. *Atmos Env.* **1984**, No. 18, 417–430.

(84) Zhang X, M. P. Theoretical Analysis of Evaporative Losses of Adsorbed or Absorbed Species during Atmospheric Sampling. *Env. Sci Technol* **1991**, No. 25, 456–459.

(85) Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. Indoor and Outdoor Air Concentrations and Phase Partitioning of Perfluoroalkyl Sulfonamides and Polybrominated Diphenyl Ethers. *Env. Sci Technol* **2004**, *38* (5), 1313–1320.

(86) Zhang, X.; McMurry, P. H. Theoretical Analysis of Evaporative Losses of Adsorbed or Absorbed Species during Atmospheric Aerosol Sampling. *Environ. Sci. Technol.* **1991**, *25* (3), 456–459. https://doi.org/10.1021/es00015a012.

(87) Venkataraman, C.; Lyons, J. M.; Friedlander, S. K. Size Distributions of Polycyclic Aromatic Hydrocarbons and Elemental Carbon. 1. Sampling, Measurement Methods, and Source Characterization. *Environ. Sci. Technol.* **1994**, *28* (4), 555–562. https://doi.org/10.1021/es00053a005.

(88) Choo, G.; Kim, D.-H.; Kim, U.-J.; Lee, I.-S.; Oh, J.-E. PBDEs and Their Structural Analogues in Marine Environments: Fate and Expected Formation Mechanisms Compared with Diverse Environments. *J. Hazard. Mater.* **2018**, *343*, 116–124. https://doi.org/10.1016/j.jhazmat.2017.09.026.

(89) Hoppel, W. A.; Frick, G. M.; Larson, R. E. Effect of Nonprecipitating Clouds on the Aerosol Size Distribution in the Marine Boundary Layer. *Geophys. Res. Lett.* **1986**, *13* (2), 125–128. https://doi.org/10.1029/GL013i002p00125.

(90) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDE Technical Flame-Retardant Mixtures. *Environ. Sci. Technol.* **2006**, *40* (20), 6247–6254. https://doi.org/10.1021/es060630m.

(91) Peng, J.; Wu, D.; Jiang, Y.; Zhang, J.; Lin, X.; Lu, S.; Han, P.; Zhou, J.; Li, S.; Lei, Y.; et al. Spatiotemporal Variability of Polybrominated Diphenyl Ether Concentration in Atmospheric Fine Particles in Shenzhen, China. *Environ. Pollut.* **2018**, *238*, 749–759. https://doi.org/10.1016/j.envpol.2018.03.076.

(92) Harner, T.; Shoeib, M. Measurements of Octanol-Air Partition Coefficients (Koa) for Polybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. *J. Chem. Eng. Data* **2002**, *47*, 228–232. https://doi.org/10.1021/je010192t.

(93) Lewis, E. R.; Stephen E.; Schwartz, S. E. *Sea Salt Aerosol Production: Mechanisms, Methods, Measurements, and Models*; 2004.

(94) Webster, T. F.; Harrad, S.; Millette, J. R.; Holbrook, R. D.; Davis, J. M.; Stapleton, H. M.; Allen, J. G.; Mcclean, M. D.; Ibarra, C.; Abdallah, M. A. E.; et al. Identifying Transfer Mechanisms and Sources of Environments Using Environmental Forensic Microscopy. *Environ. Sci. Technol.* **2009**, No. 43, 3067–3072. https://doi.org/10.1021/es803139w.

(95) Cai, M., Ma, Y., Xie, Z., Zhong, G., Möller, A., Yang, H., Sturm, R., He, J., Ebinghaus, R., Meng, X.-Z.; Cai, M.; Ma, Y.; Xie, Z.; Zhong, G.; Möller, A.; Yang, H.; Sturm, R.; He, J.; Ebinghaus, R.; et al. Distribution and Air-Sea Exchange of Organochlorine Pesticides in the North Pacific and the Arctic. *J. Geophys. Res.* **2012**, *117* (D06311), 1–9. https://doi.org/10.1029/2011JD016910.

(96) Wania, F. Assessing the Potential of Persistent Organic Chemicals for Long-Range Transport and Accumulation in Polar Regions. *Environ. Sci. Technol.* **2003**, *37* (37), 1344–1351. https://doi.org/10.1021/es026019e.

5 Analysis of polybrominated diphenyl ethers in Atlantic fish samples

5.1 Abstract

Newfoundland and Labrador (NL) marine fish stocks are susceptible to bioaccumulation effects from polybrominated biphenyl ethers (PBDE) in the Gulf of St. Lawrence and the surrounding Atlantic Ocean. Consequently, these fish expose coastal inhabitants to these persistent organic pollutants (POPs) that may make them more susceptible to disease. Atlantic cod (*Gadus morhua*) and Greenland halibut/turbot (*Scophthalmus maximusfish*) livers were collected from two independent fish surveys (1993 and 2014) to assess PBDE and MeO-BDE quantities along the coasts and oceanic depths of Newfoundland island. Greater PBDE concentrations from 1993 cod fish livers compared to 2014 samples may have been influenced by recent NL landfill remediation reform and the Stockholm convention restrictions on PBDE use. The gradual reduction of PBDEs in cod fish retrieved from the Gulf of St. Lawrence to the Atlantic Ocean, and longitudinal coordinates approaching the open Atlantic Ocean may be more an effect of contaminant dilution instead of the consequence of long range transport (LRT). Greenland halibut may contain higher PBDE levels associated with oceanic depth where sediment is a known pool for these analytes. Conversely, Atlantic cod had greater PBDE and MeO-BDE contamination than Greenland halibut which may be attributed to fish lifecycle, niche range, or sampling artifact relating cod fish proximity to pelagic phytoplankton that is a known MeO-BDE producer.

5.2 Introduction

Environmental polybrominated diphenyl ethers (PBDEs) may originate from the use and breakdown of commercial products and as methoxy (MeO-BDE) and hydroxy (OH-BDE) congeners that are naturally produced and released from sponges, blue mussels and phytoplankton[1,2]. Haraguchi *et al.*[3] presented evidence that MeO-BDE in contaminated fish were linked to the presence of these congeners in human serum. A Newfoundland island study by Sarkar *et al.*[4] showed a spatial trend of anthropogenic PBDE (BDE-28 and BDE-153) levels in serum levels of coastal inhabitants suffering from chronic thyroid impairments that was suspected to be caused by a spatial difference in contamination of consumed fish. PBDEs and their congeners can compete for thyroid binding sites in humans as their analogous structure can inhibit endocrine pathways[5–7]. Marine fish may either remove the more water soluble OH-BDE contaminant through urinary excretion or methylate their bioactive alcohol functional groups into a more bioaccumulative MeO-BDE congener[5,8–12]. PBDE marine biota concentrations can range from pg/g to ng/g with MeO-BDE concentrations at similar or somewhat higher levels[13]. Kim *et al.*[9] found elevated levels of 2'-MeO-BDE-68 in microorganisms and sponges that benefit from resistance to *E. coli, Bacillus subtilus*, and *Staphylococcus aureus* conferred by MeO-BDEs[14–17]. Some marine bivalve mollusks have benefitted from this microbial resistance by incorporating MeO-BDEs from sediment and have evolved slow metabolic rates to maintain these high PBDE levels[18,19].

As persistent organic pollutants (POPs), PBDEs are resistant to environmental degradation and are subject to bioaccumulation and biomagnification[10,20]. Individual organism concentrations increase when PBDE levels biomagnify as predators consume contaminated prey of lower trophic levels. For this reason, PBDEs and MeO-BDEs are found at higher levels in high trophic level fish species such as cod fish[9,11,21–23]. Atlantic cod fish (*Gadus morhua)* and Greenland halibut/turbot (*Scophthalmus maximusfish*) are consumed globally and have been a traditional economic revenue for Newfoundland and Labrador (NL) fisheries. This cod species can be a key indicator of PBDE contamination in the Atlantic Ocean since their POP levels are generally higher than most Arctic fish species. Numerous open water prey fish including capelin (*Mallotus villosus*) are the main diet of Atlantic cod. Greenland halibut has also been known to prominently prey on pelagic fish, as well as cod fish, and consuming shrimp and blue mussels that reside on the sediment layer[24,25]. In turn, Atlantic cod and Greenland halibut are known food staples for white whales, cephalopods, and narwhals[26]. The migration of both fish species is dependent on their spawning behaviors and on their prey migration schedule (e.g. capelin), therefore, limiting their niche to a given region along the NL coast[27]. Given their recorded lifespan to be close in age, it could show that the same Atlantic cod (~25 years[27]) and Greenland halibut (~30 years[28]) fish stocks may be able to interact within the same niche.

Atlantic cod and Greenland halibut reside primarily in the cold oceanic benthic region as apex predators. However, Greenland halibut will spend a greater fraction of their lives in the sediment regions than cod fish, thus may occupy slightly different food

webs and be exposed to different PBDE/MeO-BDE pools[1,23,29,30]. Although trophic level is an important consideration to PBDE concentrations, the location of fish may also play a role. Surface waters (Table 1-1) may harbor seasonal phytoplankton with the potential for MeO-BDE production and can be exposed to atmospheric anthropogenic PBDE deposition, both of which could be possible exposure routes for marine organisms. Marine sediments (Table 1-2) are known to accumulate PBDEs and their analogues; hence, benthic organisms including Greenland halibut with natural niches in these regions could develop an additional route of exposure[29–32].

PBDE assessments have recently been applied to cod fish species and numerous benthic fish[33] with MeO-BDE monitoring being relatively new with initial marine analysis in seal and fish (1981, 1988)[34]. Hung *et al.*[35] showed that contributions to long range transport (LRT) of PBDE from the atmosphere (previously discussed in Chapter 4) were comparable to transport systems through marine fish migrations. This study will be the first to assess both the anthropogenic PBDE and MeO-BDE content in coastal Atlantic cod and Greenland halibut that are historically a staple of commercialized fishing in NL. In this work, these aspects will be demonstrated: (1) how PBDE manufacturing affects PBDE and MeO-BDE levels in fish collected before and after the international ban; (2) the longitudinal and ocean depth spatial distribution of PBDE and MeO-BDE in fish liver from the Gulf of St. Lawrence and the Atlantic Ocean; and (3) how differing ecological food web niches of Atlantic cod and Greenland halibut contribute to PBDE and MeO-BDE levels in the Atlantic Ocean.

5.3 Materials and methods

5.3.1 Chemicals

Analytical standards and chemicals were purchased as described in Chapter 2.

5.3.2 Sample collection

Liver samples of two Atlantic fish species, Atlantic cod (*Gadus Morhua*) and Greenland halibut (*Scophthalmus maximusfish*) were obtained from a 2014 fish survey (Figure 5-1) conducted by the Marine Institute of Memorial University in the open Atlantic Ocean off the eastern and south eastern (latitude: 47 to 50° N, longitude: 52 to 45 ° W) coasts of the island of Newfoundland. Atlantic cod samples were collected on 2 separate occasions by the Department of Fisheries and Oceans Canada (DFO): (1) a 2014 survey in the Canadian coast guard fisheries ship (CCGS) Teleost; and (2) a 1993 survey on a ship via net trawling. These fish samples were collected by trawling nets through oceanic pelagic and benthic regions. Recreationally caught Atlantic cod fish from two sampling sites (Placentia Bay, SE coast and Hamilton Sound, NE coast) caught by jigging (anchored hooks disguised as fish meant to catch benthic fish) were also included in this study. For all samples, livers were extracted on boats immediately after fish were captured.

Archived samples from the 1993 collection were shipped as homogenized liver samples in glass screw jars. All fish samples were stored in Ziploc® bags at -18 °C prior to analysis**.** Since samples were in cold storage and in the dark (minimized photolysis; the main PBDE degradation pathway), the PBDE analyte was likely intact within the sample

despite the slow degradation of fish matrix by enzyme and bacteria activity[36]. Therefore, fish samples can be stored for many years in freezer temperatures.

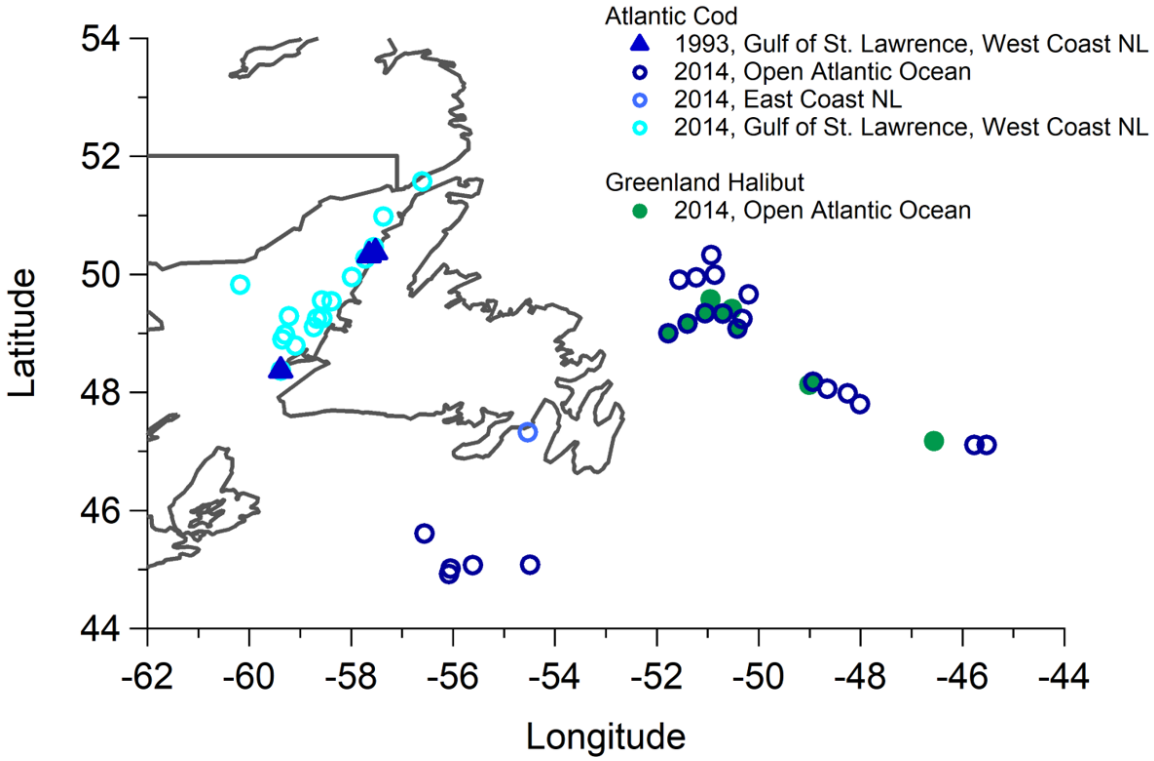

Figure 5-1. Locations of fish collections in Newfoundland coastal regions conducted by Department of Fisheries and Oceans in 1993 (cod, filled dark blue triangles) and 2014 (cod, open teal circles), Memorial University Marine Institute (2014, cod, open dark blue circles and Greenland halibut, filled green circles), and recreational fishing (2014, cod, light open circles).

DFO and MUN Marine ship cruises were mainly focused on a general fish collection for the region and were not specifically seeking out Atlantic cod and Greenland halibut. Although fish diet, age, overall organism health (length, weight), regional pollutants, fishing pressure, and male/female specification are important factors that could affect PBDE and MeO-BDE bioaccumulation, specific biological information relating to the fish involved in this study were not taken consistently between samples and were omitted.

5.3.3 Sample preparation for analysis

All samples were warmed to ~10 °C in water. A ~2 g wet weight (w.w.) sample was cut with a pre-rinsed (extraction solvent) knife from the bulk fish liver and uniformly homogenized (~30 seconds) with a laboratory homogenizer before being distributed into three ~0.5 g trial runs. The homogenizer apparatus was pre-cleaned according to manufacturing guidelines with detergent and rinsed with extraction solvent before use and between samples. The internal standard BDE-118 (2.0 mg/L) stock solution was added to each fish sample aliquot (250 µL) prior to GC-MS injection. Liver samples were extracted and analyzed by GC-ECNI-MS using the methods described in Chapter 2.

5.3.4 Quality assurance

Table 5-1. Quality test of signal to noise (S/N) for triplicate ASE fish liver analysis. Each sample was extracted three times and analyzed three times. Mean ± standard deviation is shown, derived from three replicate analyses.

Fish sample trial	BDE-47	BDE-99	BDE-154
A1	11 ± 3	57 ± 5	24 ± 4
A2	15 ± 4	65 ± 5	30 ± 5
A3	18 ± 4	60 ± 8	25 ± 5
B1	15 ± 3	61 ± 7	31 ± 3
B2	15 ± 4	58 ± 4	35 ± 4
B3	19 ± 4	62 ± 7	38 ± 4
C1	16 ± 3	57 ± 8	30 ± 6
C2	15 ± 4	58 ± 5	31 ± 7
C3	14 ± 5	63 ± 4	35 ± 4

The manual liquid-liquid extraction procedure (2.3.3.1) was improved with an automated ASE™ system as described in section 2.3.3.2. Quality assurance of this ASE process was tested (Table 5-1) for consistency and precision on cod fish samples by conducting a GC-MS analysis on triplicate samples of the same cod liver sample. From one

of the triplicate samples, an additional triplicate ASE extraction was performed where identical results would yield a satisfactory test of precision.

5.4 Results and discussion

5.4.1 Temporal observations in Atlantic cod fish

5.4.1.1 Legacy PBDEs in Atlantic fish

Gulf of St. Lawrence fish collections were cod fish livers retrieved from the DFO 1993 and 2014 fish surveys. Within the 1993 fish collection, PBDE concentrations were found in the order of magnitude as BDE-47 > BDE-99 > BDE-28 and had total BDE concentrations of 3.95 – 79.5 ng/g w.w. The larger PBDE congeners (BDE-156 and BDE-209) were not found in this sample set. Fish collected in 2014 had total PBDE concentrations within a range of 0.01 – 74.4 ng/g w.w. (Table 5-2) and showed concentrations in decreasing order of BDE-47 > BDE-99 > BDE-156 > BDE-28 > BDE-209. Larger BDE-209 (1.56 ± 3.2 ng/g) and BDE-156 (2.30 ± 3.31 ng/g) were present in these samples, which might imply that they originate from nearby sources. Concentration ranges in 1993 were about 1 to 4 times greater in magnitude than their respective PBDE congeners collected in 2014. This discrepancy in fish samples archived in 1993 could be indicative of sample collections during a time prior to the PBDE manufacturing ban, although differences in cruise sampling apparatus and personnel cannot be excluded.

Table 5-2. Selected reports of PBDE and MeO-BDEs in Atlantic cod fish. Concentrations represent the sum of PBDEs unless otherwise noted.

Location	Sample Year	Fish	∑PBDE	Concentration	Reference
St. John's, NL	2014, 1993	Atlantic cod (*Gadus morhua*)	$\sum_4$PBDE: BDEs 28, 47, 99, 209, 6-MeO-BDE-47, 2'-MeO-BDE-68	$\sum_5$[PBDE]: (2014) 0.01 – 74.4, (1993) 3.95 – 79.5 ng/g w.w. $\sum_2$[MeO-BDE]: (2014) 2.67 – 41.0 ng/g w.w. (1993) 9.63 – 61.9 ng/g w.w.	This study.
Baltic Sea, North Atlantic Ocean	2017 - 1972	Atlantic cod	$\sum_{19}$PBDE: BDEs 17, 28/33, 47, 49, 66, 71, 77, 85, 99, 178, 100, 119, 126, 138, 153, 154, 180, 183, 209	Fish oil: 9.9 - 415 ng/g Canned fish: 10.5 - 13 ng/g	[37]
Barents Sea, Norway	2016 - 2006	Atlantic cod	$\sum_7$PBDE: BDEs 28, 47, 99, 100, 153, 154, 183	3.4 - 29 ug/kg w.w.	[38]
Southern Barents Sea	2015, 2012	Atlantic Cod	$\sum_{15}$PBDE: BDEs 28, 35, 47, 49/71, 66, 75, 77, 85, 99, 100, 118, 119, 138, 153, 154	2012: 6.6 ± 2.0 µg/kg 2015: 5.6 ± 1.9 µg/kg	[23]
Baltic sea	2013	Atlantic Cod, Baltic cod	$\sum_{33}$PBDE: BDEs 1, 2, 3, 10, 7, 11, 8, 12, 13, 15, 30, 32, 17, 25, 33, 35, 37, 75, 77, 71, 47, 66, 110, 119, 116, 85, 126, 155, 153, 154, 166, 183, 209 3-MeO-BDE-28, 3-MeO-BDE-47, 5-MeO-BDE-99, 3-MeO-BDE-154	∑PBDE: 57.857 ± 30,672 pg/g ∑MeO-BDE: 5441 ± 2918 pg/g	[39]

Table 5-2 (cont'd). Selected reports of PBDE and MeO-BDEs in cod fish. Concentrations represent the sum of PBDEs unless otherwise noted.

Location	Sample Year	Fish	∑PBDE	Concentration	Reference
Hudson Bay	2012	Arctic Cod (*B. Saida*)	2'- MeO-BDE-28, 4'-MeO-BDE-17, 2'-MeO-BDE-75, 6-MeO-BDE-47, 2'-MeO-BDE-74, 6'-MeO-BDE-66	9.9 (3.3 – 30) ng/g w.w.	32
St. Lawrence River	2012, 2008	Yellow perch *(P. flavescen)*, Northern pike (*E. Lucius*), Muskell-unge (*E. masquinongy*)	$\sum_5$PBDE: BDEs 47, 99, 100, 49, 153	Yellow perch: 94 & 2480 ng/g w.w. Northern pike: 1068 & 5971 ng/g w.w. Muskellunge: 696 & 24,031 ng/g w.w.	40
Barents Sea	2014-2013, 2011-2009, 2007-2006	Arctic cod	$\sum_7$PBDE: BDEs 28, 47, 99, 100, 153, 154, 183	4.5 ± 3.5, 1.8 – 12.8 ug/kg w.w.	41
Norwegian Coast	2007	Atlantic cod	$\sum_5$PBDE: BDEs 28, 47, 100, 99, 154	Oksfjord: 20.5 ± 22.6 ng/g w.w., Hitra: 37.6 ± 27.4 ng/g w.w., Ryfylke: 42.9 ± 33.3 ng/g w.w.	30
North East Atlantic Ocean	2006	Atlantic cod	$\sum_7$PBDE: BDEs 28, 47, 99, 100, 153, 154, 183	0.2 - 143 µg/kg	29
St. Lawrence Estuary	2003	Atlantic cod	$\sum_{15}$PBDE: BDEs 17, 28, 33, 35, 47, 49, 99, 100, 126, 138, 153, 154, 155, 183, 190	30.4 ng/g w.w.	42
Davis Strait, Eastern Canadian Arctic	2001, 2000	Arctic cod	$\sum_7$PBDE: BDEs 47, 85, 99, 100, 153, 154, 209	23 ± 13 ng/g	43

Table 5-2 (cont'd). Selected reports of PBDE and MeO-BDEs in cod fish. Concentrations represent the sum of PBDEs unless otherwise noted.

Location	Sample Year	Fish	∑PBDE	Concentration	Reference
Barents Sea, Eastern Canadian Arctic	2001, 2000	Polar cod (*B. Saida*)	$\sum_9$PBDE: BDEs 28, 47, 71, 77, 99, 100, 153, 154, 183	23 ng/g w.w.	1
Svalbard, Norway	1999, 1989	Polar cod	$\sum_6$PBDE: BDEs 28, 47, 99, 100, 154, 209	BDE-47: 0.066 ng/g w.w. BDE-99: 0.0119 ng/g w.w. ∑PBDE: 1.99 ± 1.19 ng/g w.w.	26
Hudson Bay, Canada	1999 - 2003	Arctic cod (*B. saida)*	2'-MeO-BDE-68 6-MeO-BDE-47 $\sum_{11}$PBDE: BDEs 3, 47, 99, 15, 28, 47, 77, 118, 100, 153, 183	∑MeO-BDE: 9.9 (3.3 - 30) ng/g w.w. ∑PBDE: 9.8 (2.6 - 36) ng/g w.w.	32
Swedish Baltic coast	1990 - 2004	Perch (*P. fluviatilis*)	6-MeO-BDE47, 2'-MeO-BDE-68, 6-MeO-BDE-85, 6-MeO-BDE-90, 6-MeO-BDE-99	34 ng/g lipid	44
Barents Sea coast	1992, 1993, 1998	Arctic cod liver	$\sum_7$PBDE: BDEs 15, 28, 47, 66, 99, 100, 153	1992: 16, 390, 905 pg/g 1993: 1210 and 9955 pg/g 1998: 14 – 1210, 311 – 16,390 pg/g	45

*DL = detection limit
*w.w. = wet weight

Distribution patterns of PBDE congeners (Figure 5-2) showed higher concentrations in the 1993 fish survey than 2014 results, with a greater proportion of the smaller PBDE congeners (BDE-28 and BDE-47) in 1993 and a greater abundance of relatively larger PBDE congeners (BDE-99, BDE-156, and BDE-209) in 2014. The presence

of more brominated PBDE congeners in 2014 may be the trailing result of the preliminary PBDE manufacturing ban that initially removed penta-BDE mixes before larger PBDE mixes were phased out. The great presence of lower brominated BDE-47 within both sample years may have been a product of degraded components of higher brominated congeners in addition to the already prolific BDE-47 pool of the manufactured penta-BDE mix. The bioavailability of these lower PBDE have also contributed to its longer half lives within organisms. Mizukawa *et al.*[20] showed that BDE-47 and BDE-154 maintained their structure within marine biota.

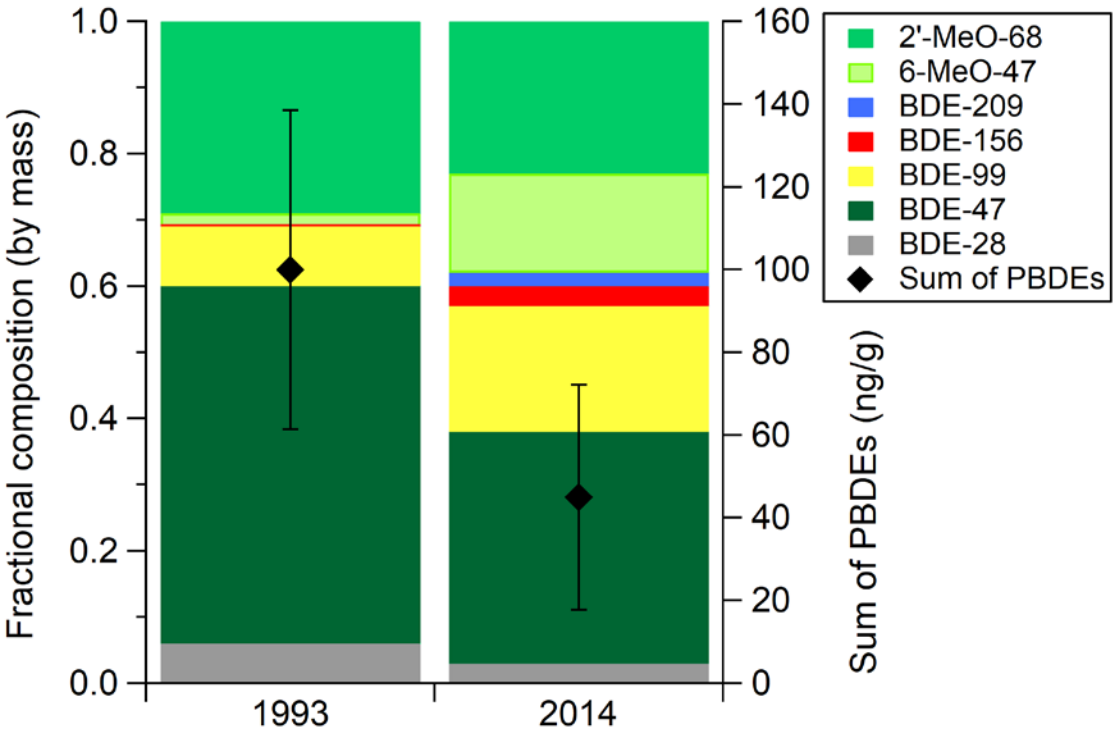

Figure 5-2. Total PBDE and MeO-BDE concentration distribution in Atlantic cod fish liver collected in the Gulf of St. Lawrence. Error bars represent the standard deviation of the average PBDE concentrations for the specific year of samples collected.

5.4.1.2 Temporal MeO-BDE fish observations

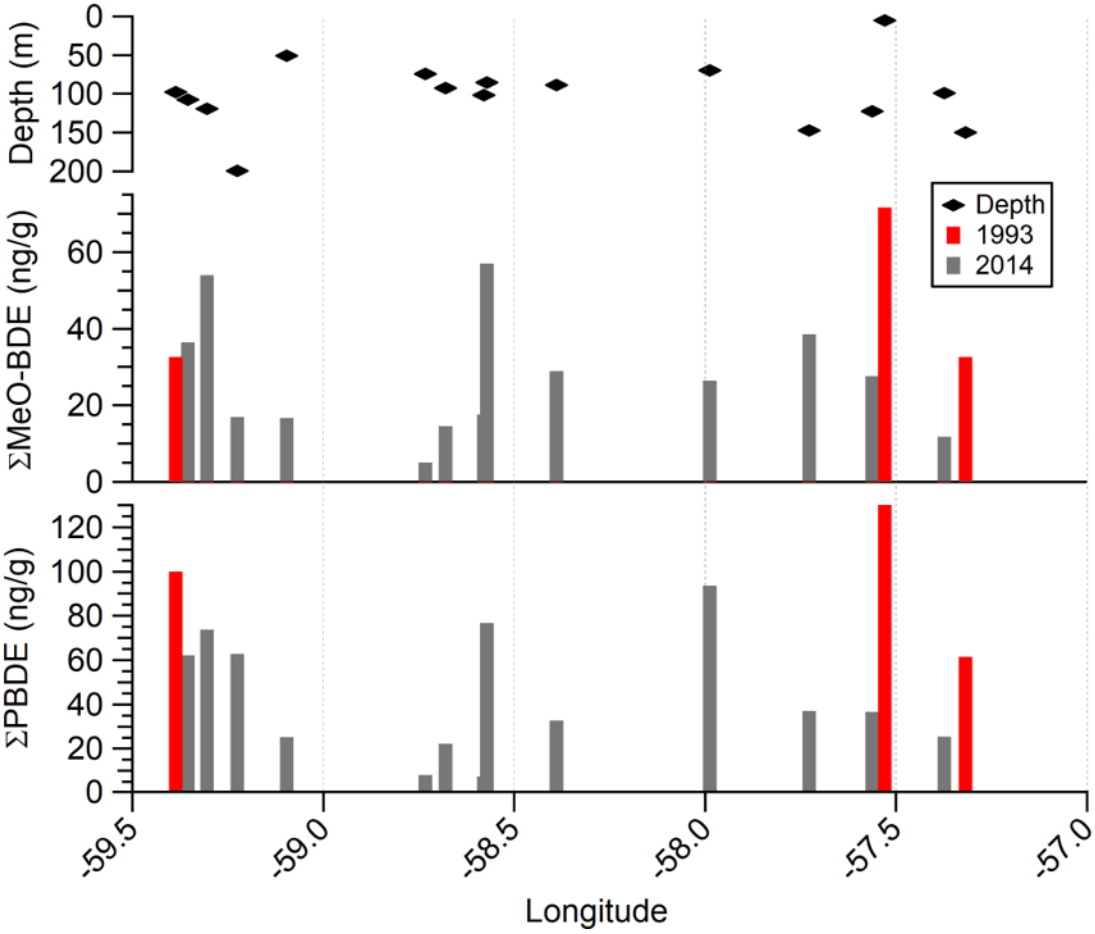

Figure 5-3. PBDE accumulation in Atlantic cod liver from the 1993 and 2014 Gulf of St. Lawrence fish survey.

Cod fish MeO-BDE concentrations from 1993 (9.63 – 61.9 ng/g w.w., Appendix C, Table C-3) were greater than 2014 (2.67 – 41.0 ng/g w.w., Appendix C, Table C-4) sample periods. Although 1993 fish liver samples may not be fully representative of the population because of the few liver samples (N = 3) collected, the geographical location (Figure 5-3) of fish collections ranged from the north and southern outer limits of the fish sampling region on the Gulf of St. Lawrence may represent an impression of the area**.** Prevailing concentrations were found as follows for 1993: BDE-47 > MeO-68 > BDE-99 >

BDE-28 > MeO-47; and 2014: BDE-47 > BDE-99/MeO-68 > MeO-47 > BDE-156 > BDE-28 > BDE-209. (2014). Choo *et al.*[46] showed similar MeO-BDE levels in biota (0.103 – 13.3 ng/g w.w. in bivalves) that were greater than anthropogenic PBDEs (N.D. to 0.254 ng/g w.w.), which tend to be greater in sediment and marine environments. Löfstrand *et al.*[47] indicated that MeO-BDE concentrations may be a product of seasonal algae growth. Blue mussels predominately gain biomass through filter feeding of these algae and phytoplankton, thus during warmer seasons of intense primary production blue mussels were likely to thrive. Chlorophyll-*a* is commonly monitored by satellite and used to represent phytoplankton productivity. This could be used as a proxy to understand the spatial and seasonal distribution of MeO-BDE production.

Phytoplankton primary production (Figure 5-4) increases with agricultural fertilizer run off and land fill leachate that may intensify MeO-BDE production and anoxic conditions. Sanctioned by the Environment Protection Act, NL executed the Province's Waste Management Strategy (2002) followed by an Implementation Plan (2007) to commission environmentally sustainable landfills and develop infrastructure to reduce the total incoming waste to these landfills by 50%. A survey showed that 30% of this waste consisted of organics[48]. Fish samples collected in 1993 may have been influenced by increased phytoplankton primary production and subsequent MeO-BDE exposure from urban run off prior to this waste reduction project, where lower MeO-BDE levels in 2014 fish samples may be the effect of this waste remediation. Correspondingly, Sinkkonen *et. al.*[45] shown that MeO-tetra-BDE concentrations in Arctic cod liver retrieved from the

Vestertana Fjord near the Atlantic Ocean had reported higher concentrations in earlier samples (1992, 1993) than in samples collected early (1987-1991) and later (1998).

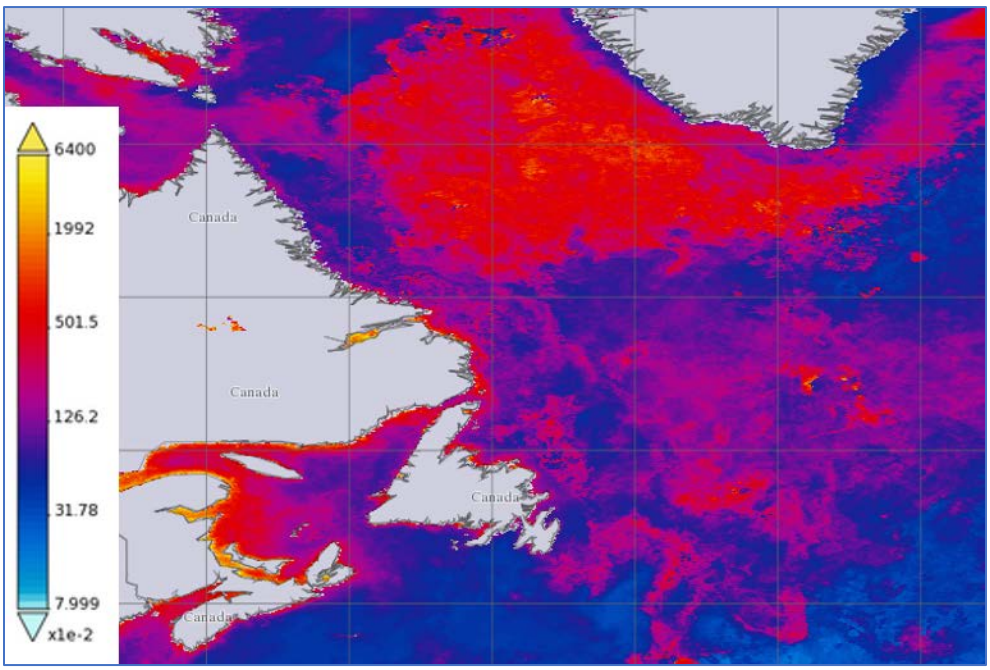

Figure 5-4. Chlorophyll *a* (Chl *a*) measured by MODIS (Moderate Resolution Imaging Spectroradiometer) from Terra (EOS AM) and Aqua (EOS PM) satellites facilitated by Giovanni NASA version 4.30 website. Chl *a* (mL/m^3, monthly recordings) was measured for the month of August 2014. Data is retrieved from the National Oceanic and Atmospheric Administration (NOAA)[49].

5.4.2 Spatial trends in Atlantic fish

5.4.2.1. PBDE

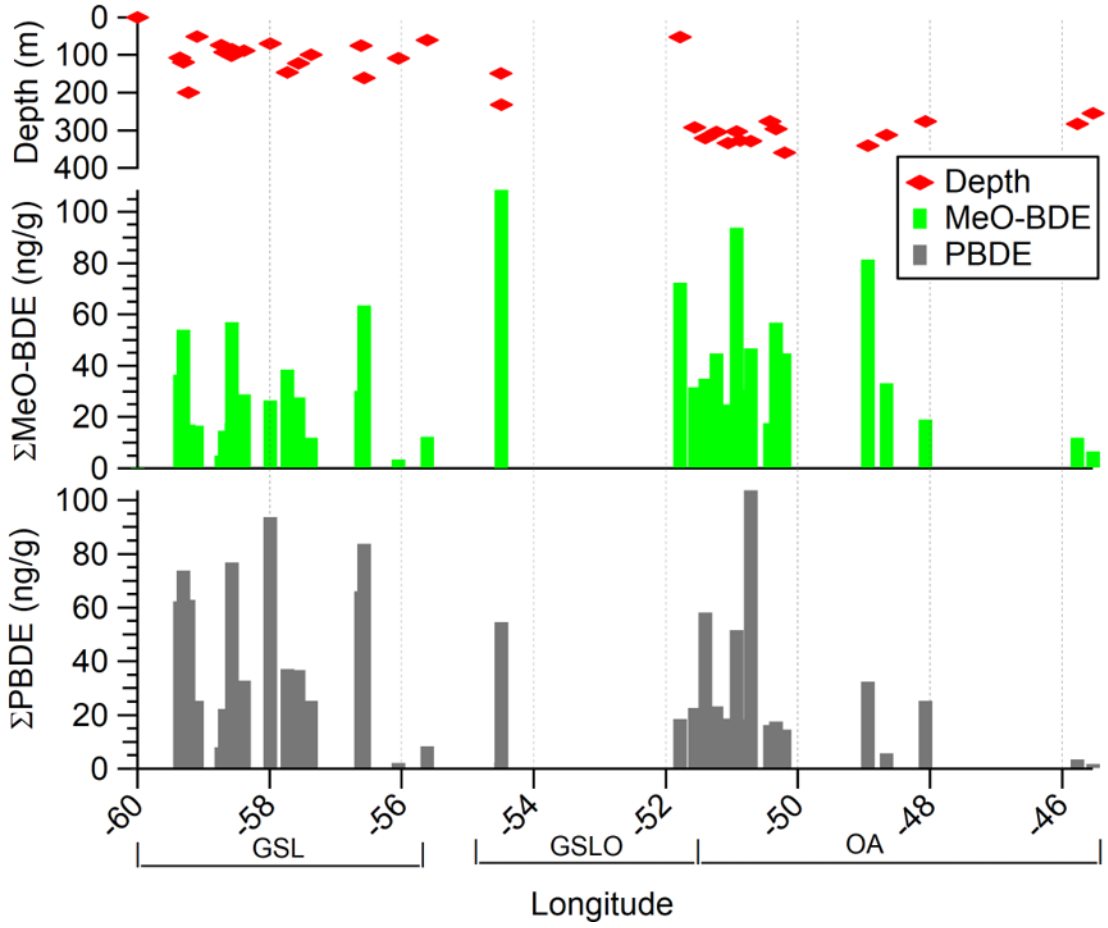

Figure 5-5. Survey (2014) of PBDE and MeO-BDE accumulation in Atlantic cod liver collected from NL coastal regions and their corresponding surface depth profile. Fish collections were retrieved from the Gulf of St. Lawrence (GSL), Gulf of St. Lawrence (GSLO), and the Atlantic Ocean (AO).

The sum of anthropogenic PBDE in cod fish livers (Figure 5-5, Appendix C) ranged from (0.01 - 74.4 ng/g, N = 34) w.w. across all 2014 fish surveys. These results were comparable to values of other marine fish studies in Table 5-2. According to a t-test analysis (*f*-ratio = 3.51, p = 0.07), anthropogenic PBDEs levels in cod fish samples from the Gulf of St. Lawrence (Figure 5-6, 44.95 ± 27.20 ng/g w.w.) were higher than those in the Atlantic Ocean (26.91 ± 9.58 ng/g w.w.). In terms of this analysis, the sample region of the

Gulf of the St. Lawrence outlet was not considered in this comparison between regions because of the relatively small sample size. Cod liver concentrations of BDE-209 (1.82 ± 3.80, 0.78 – 12.5 ng/g w.w.) from the Atlantic Ocean and St. Lawrence cod fish results (1.56 ± 3.2, 0.84 – 10.5 ng/g w.w.) were statistically similar (*f*-ratio = 0.04, *p* = 0.84). Although PBDE and MeO-BDE levels in Atlantic cod showed no correlation with their longitudinal coordinates (Table 5-3) within the Gulf of St. Lawrence, cod fish results (Figure 5-6) displayed a general relationship with NL coastal regions as a whole. Similar to the Baltic Sea, the St. Lawrence river is surrounded by industrial and urban sources that may be subjected to a greater anthropogenic PBDE exposure, thus a greater potential for bioaccumulation of PBDEs within local marine biota may be expected closer to coastal regions[50]. Nøstbakken *et al.*[29] showed BDE-47 levels in fish collected with increasing distance from coastal regions. The contaminant levels in this study may be consistent with dilution effects rather than LRT as suggested by other studies[29,51].

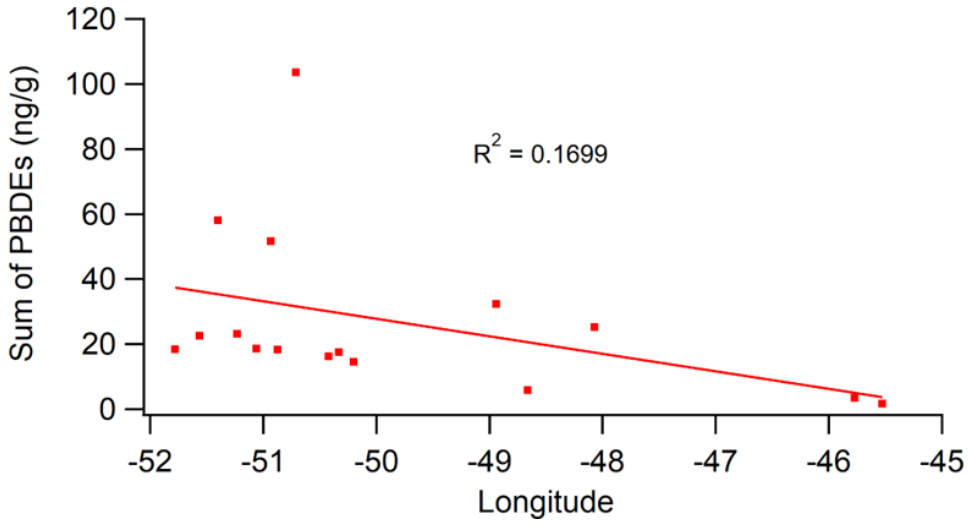

Figure 5-6. Accumulated PBDEs (*f*-ratio = 3.51, p = 0.07) in Atlantic cod liver from NL eastern coastal region to the open Atlantic Ocean.

Table 5-3. Relationship between longitude and concentrations of PBDE and MeO-BDE in Atlantic cod.

Location	Analyte	Sample size	R^2	p-value	Sign of the slope
St. Lawrence River	∑PBDE	14	N/A	N/A	N/A
	∑MeO-BDE		0.006	0.784	-
Atlantic Ocean	∑PBDE	16	0.170	0.100	-
	∑MeO-BDE		0.227	0.053	-

According to the PBDE congener distribution in Figure 5-7 and Figure 5-8, BDE-47 was the most abundant anthropogenic congener in these fish samples. BDE-47 and other anthropogenic PBDEs that were observed in these fish samples were commonly observed in high level trophic marine organisms of other studies[32,52]. These lower PBDE intermediates (BDE-28, BDE-47, BDE-99, and BDE-156) may also be a result of the larger brominated BDE-209 photolysis on surface water as remnants percolate into fish niches within the water column[53–55]. Due to the larger sample size of Atlantic cod (N = 38) throughout the longitudinal span of this study in comparison to the Greenland halibut (N = 8), total PBDE concentration trends in fish were more characteristic of Atlantic cod fish. PBDEs that are lower brominated congeners than the tetra-BDE class are not considered as being of great environmental importance and may not be accounted for in the majority of PBDE studies[39].

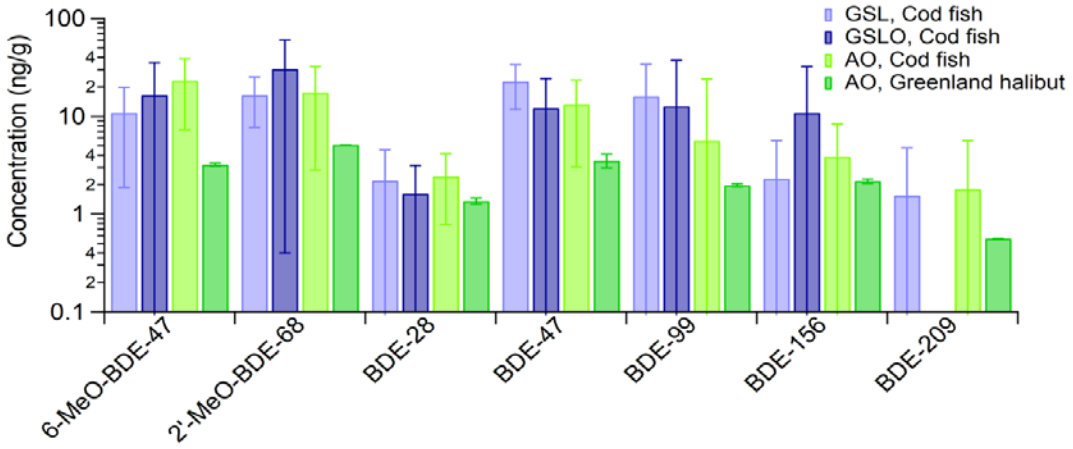

Figure 5-7. PBDE and MeO-BDE concentrations in Atlantic cod fish liver collected in 2014. Fish collections were retrieved from the Gulf of St. Lawrence (GSL), Gulf of St. Lawrence Outlet (GSLO), and the Atlantic Ocean (AO). Error bars represent the standard deviation of the average PBDE and MeO-BDE concentrations for the sampled region.

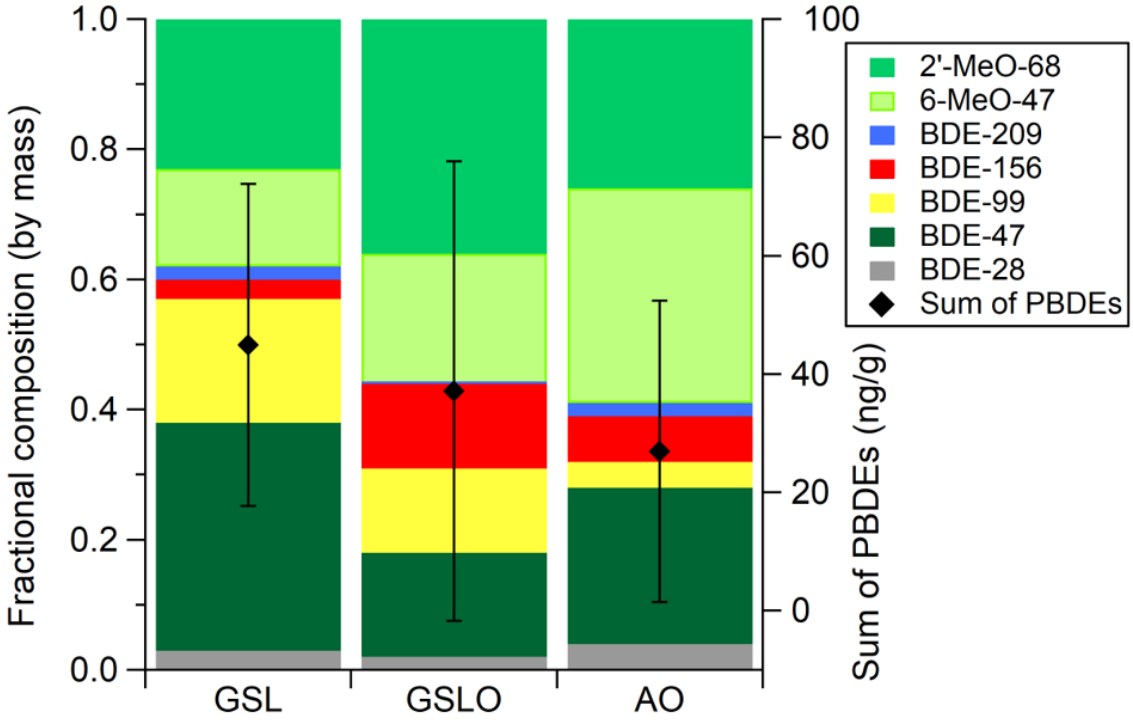

Figure 5-8. PBDE and MeO-BDE distribution in Atlantic cod fish liver collected in 2014. Fish collections were retrieved from the Gulf of St. Lawrence (GSL), Gulf of St. Lawrence Outlet (GSLO), and the Atlantic Ocean (AO). Error bars represent the standard deviation of the average PBDE concentrations for the sampled region.

5.4.2.2 MeO-BDE

T-test analysis (*f*-ratio = 13.79, $p < 0.01$) of MeO-BDE trends (Figure 5-7) showed a correlation between cod fish concentrations and longitude from the St. Lawrence river (2.56 – 36.1 ng/g w.w.) bearing towards the river outlet (2.67 – 42.9 ng/g w.w.) and the open Atlantic Ocean (0.13 – 62.1 ng/g w.w.). Considering the immense surface area and vast resource of global oceans as a source for natural MeO/OH-BDE production and their recent discovery, environmental concentrations may be underestimated[56]. Figure 5-9 further illustrated that MeO-BDE concentrations not only decrease between the Gulf of the St. Lawrence and the Atlantic Ocean but also decrease with increasing longitudinal distance from coastal shores. Urban and agricultural runoff may be contributing factors to phytoplankton primary production and subsequent MeO-BDE production. Rotander *et al.*[57] found 6-MeO-BDE-47 to be as ubiquitous in marine biota as its anthropogenic BDE-47 counterpart. Other southern hemisphere studies showed greater anthropogenic PBDE concentrations in aquatic biota (birds, fish, Cetacea) than MeO-BDEs[58–60]. From this research, MeO-BDE production through summer primary production may contribute significantly to oceanic pools, whereas anthropogenic PBDE may be a product of mainland LRT effects.

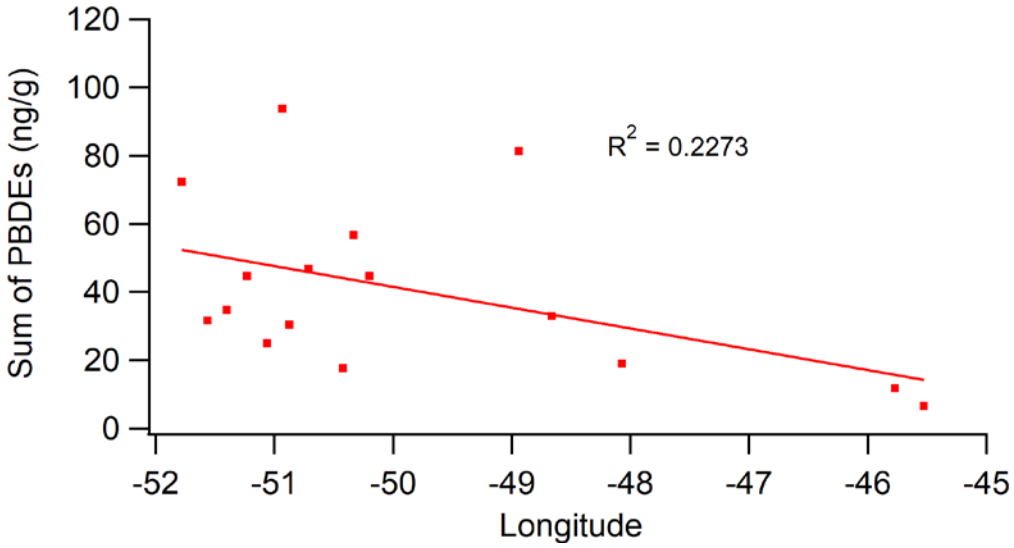

Figure 5-9. Accumulated MeO-BDE (*f*-ratio = 13.79, $p < 0.01$) in Atlantic cod liver from NL eastern coastal region to the open Atlantic Ocean.

Degradation routes of MeO-BDE products within fish metabolism include sequential bromine loss as resultant congeners with three or more neighboring bromine substituents are debrominated[44]. The biotransformation of anthropogenic PBDEs into MeO-BDE is an improbable occurrence and will likely favor urinary excretion. The only known pathway for MeO-BDE congeners to be derived from anthropogenic sources may occur in instances where fish become overwhelmed with a direct application of concentrated PBDE (ppm) dose compared to ppt levels found in marine environments[13,34].

5.4.2.3 Depth profile

Table 5-4. Ocean depth profile of PBDE and MeO-BDE in sampled NL marine fish.

Location	Analyte	Max. ocean depth range (m)	Sample size	R^2	p-value
St. Lawrence River (Atlantic cod)	∑PBDE, 1993	5.0 – 150.0	3	0.0089	N/A
	∑PBDE, 2014	50.5 – 199.5	14	0.0155	0.658
	∑MeO-BDE, 2014			0.0112	0.708
Atlantic Ocean	∑PBDE, cod	51.8 – 359.2	16	0.0444	0.417
	∑MeO-BDE, cod			0.0189	0.599
	∑PBDE, halibut	276.7 - 736.0	8	0.7969	0.0012
	∑MeO-BDE, halibut			0.0024	0.900

Fish samples were acquired via net trawling from a group of underwater plateaus that include the Grand Banks of NL (15 – 91 m deep) and Flemish Cap (122 m deep) near the northwest Atlantic mid-ocean canyon (100 – 200 m deep). The PBDE concentrations (Table 5-4) in marine fish with respect to ocean depth showed no correlation. Although anthropogenic PBDEs in Greenland halibut from the open Atlantic Ocean was the only significant depth trend, Figure 5-10 shows that this trend was driven by a fish sample captured in the deepest region within a relatively small sample size and could be anecdotal. Anthropogenic PBDE concentrations (0.04 – 16.5 ng/g w.w.) with BDE-209 (0.56 ± 1.30, 0.77 – 3.88 ng/g w.w.) were similar to other benthic fish studies (Table 5-5). Greenland halibut inhabit a small niche in the deep sea floor where POPs, specifically BDE-209, are known to be prevalent. Although NL waste management has improved since the

early 2000s, local dumping of used manufacturing goods that may contain brominated fire retardants remains a large problem[61].

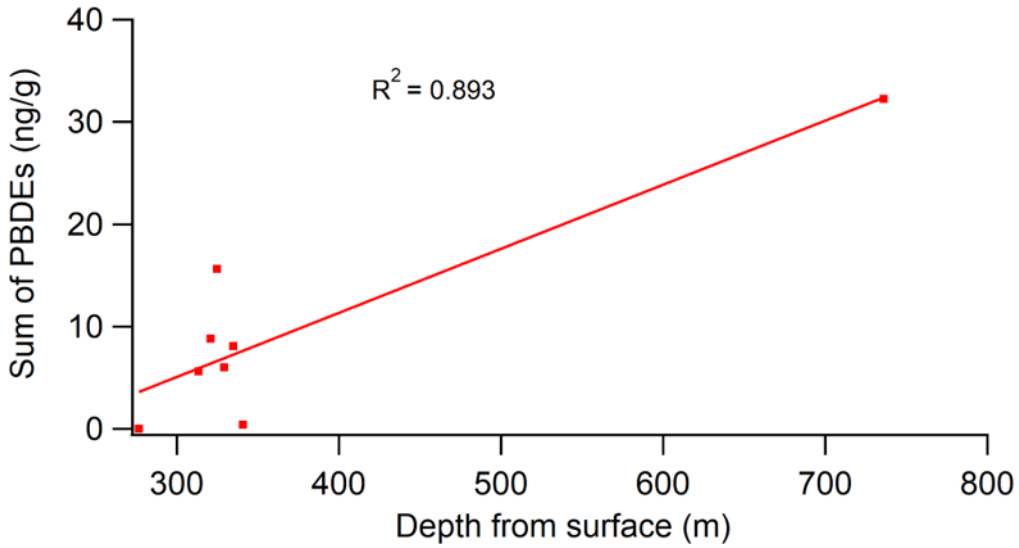

Figure 5-10. PBDE accumulation (p = 0.0012) in Greenland halibut fish liver with respect to oceanic depths from collection sites in the open Atlantic Ocean.

Table 5-5. Selected reports of PBDE and MeO-BDE in benthic fish.

Location	Sampling Year	Benthic Fish	∑PBDE	Concentration	Reference
North East Atlantic Ocean	2016 - 2006	Greenland Halibut (*Hippoglossus Hippoglossu*)	$\sum_7$PBDE: BDEs 28, 47, 99, 100, 153, 154, 183	2.0 µg/kg	29
North Sea	2015, 2012, 2009	Haddock (*M. aeglefinus*)	$\sum_{15}$PBDE: BDEs 28, 35, 47, 49/71, 66, 75, 77, 85, 99, 100, 118, 119, 138, 153, 154	2015: 2.1 ± 1.3 ug/kg 2012: 3.1 ± 1.3 ug/kg 2009: 4.8 ± 1.6 ug/kg	23
North Sea	2013, 2012	Dab (*L. limanda*)	$\sum_8$PBDE: BDEs 28, 47, 66, 99, 100, 153, 154, 183	146 ± 81 pg/g w.w.	33
Western Scheldt	2010	European flounder (*P. flesus*), Common sole (*S. solea*)	$\sum_7$PBDE: BDE 28, 47, 99, 100, 153, 154, 183	1.19, 0.25-3.97	62
S. Baltic Sea	2009	Flounder (*P. flesus*)	$\sum_7$PBDE: BDEs 28, 47, 100, 99, 153, 154, 183	0.0085 ug/kg w.w.	63
St. Lawrence Estuary	2003	Greenland Halibut (*R. hippoglossoides*)	$\sum_{10}$PBDE: BDEs 28, 47, 49, 66, 99, 100, 153, 154, 155, 183	$\sum_{10}$PBDE: 27.9 ng/g w.w.	42
St. Lawrence Estuary	2000 - 1999	Greenland Halibut	$\sum_{10}$PBDE: BDEs 28, 47, 49, 66, 99, 100, 153, 154, 155, 183	$\sum_{10}$PBDE: 12 µg/kg	64
Alaska	2004 - 2003	Pacific Halibut (*H. stenolepsis*)	∑PBDE: unspecified, unpublished	DL - 22 ng/g w.w. (DL - 0.6 ng/g) Avg. 7.3 ± 9.0 ng/g w.w.	1
Svalbard, Norway	1999 - 1989	Greenland Halibut (muscle)	$\sum_2$PBDE: BDEs 47, 99	BDE-47: 0.16 ng/g w.w. BDE-99: 0.0089 ng/g w.w.	26

5.4.2.4 Atlantic fish ecosystem

According t-test analysis, total PBDE (*f*-ratio = 3.36, p = 0.08, N = 16, 26.91 ± 25.48 ng/g, 0.12 – 79.5 ng/g w.w.) and MeO-BDE concentrations (*f*-ratio = 12.59, p < 0.01, 40.59 ± 24.93 ng/g) in cod fish livers were higher than Greenland halibut liver samples of PBDE (N = 8, 9.58 ± 10.4 ng/g, 0.10 – 14.3 ng/g w.w.) and MeO-BDE (8.30 ± 7.47 ng/g w.w.). Although Boitsov *et al.*[23] demonstrated that cod fish PBDE levels were similar to halibut, this study (Figure 5-11) showed that cod fish may have been more MeO-BDE bioaccumulation with MeO-BDE levels being about 70% greater than anthropogenic PBDE results. Phytoplankton blooms (Figure 5-4) are known to span the greater surface waters from NL to Greenland, and focused regions within the Gulf of St. Lawrence. The cod fish niche are inherently in the water column under a relatively small territory of about 1 – 1.5 ha (winter) and could exceed 3 km/day from this area in the summer making these fish more susceptible to MeO/OH-BDE exposure from phytoplankton blooms and bioaccumulation from prey fish[11,32,50,65].

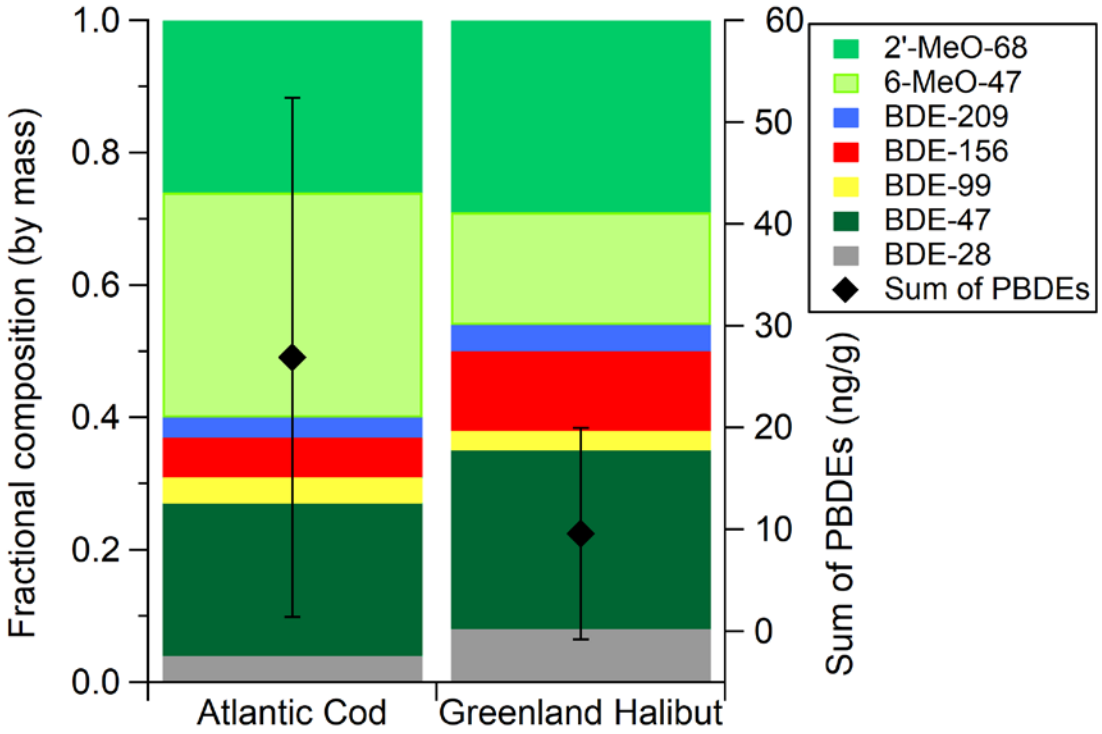

Figure 5-11. Survey of PBDE and MeO-BDE accumulation in Greenland halibut liver from the Atlantic Ocean and their corresponding surface depth profile. Error bars represent the standard deviation of the average PBDE concentrations for each fish species.

Greenland halibut samples were entirely taken from the Marine Institute Atlantic Ocean survey and consisted of anthropogenic PBDEs (0.10 – 16.5 ng/g w.w.) and MeO-BDE (0.29 – 14.3 ng/g w.w.). There was no correlation with PBDE (R^2 = 0.322, p = 0.111) or MeO-BDE (R^2 = 0.068, p = 0.497) concentrations and longitudinal coordinates from NL coastal regions. Greenland halibut concentrations are great at 47.18 N and 46.56 W (Figure 5-1), however, these results are anecdotal considering the small sample size. The lower halibut concentration (BDE-209, 0.56 ± 1.30 ng/g w.w.) compared to the cod fish (BDE-209, 1.56 ± 3.2 ng/g w.w.) result may have been attributed to Atlantic cod primary consumption of pelagic fish and migration patterns in the water column. In contrast,

Roszko *et al.*[39] found BDE-47 levels higher in Greenland halibut than polar cod, while BDE-99 had similar results. Although sediment and blue mussels may be sources of MeO-BDE production and reservoirs for anthropogenic PBDE (e.g. BDE-99)[32], marine temperatures decrease with depth and consequently inhibit blue mussels, thus exposure to MeO-BDE in Greenland halibut may have also been reduced.

5.5 Conclusions

Atlantic cod and Greenland halibut have bioaccumulated PBDEs and MeO-BDEs in regions of the Gulf of the St. Lawrence and the Atlantic Ocean. Cod liver samples collected from 1993 had greater analyte levels of PBDEs and MeO-BDEs than samples taken in 2014. These lower concentrations in the more recent samples maybe a result of the international ban on PBDE manufacturing and the remediation of NL landfills to reduce organics and subsequently reduce phytoplankton primary production associated with landfill runoff and MeO-BDE production. PBDE and MeO-BDE levels also significantly decreased with increased longitudinal distance from NL shorelines which indicated a dilution effect with increased distance from urban sources and its effect on primary production. Ocean depth profiles showed no correlation with most analyte concentrations. Greenland halibut samples seem to have a greater PBDE content in deep ocean regions, however this trend may have been motivated by a single fish sample. MeO-BDE in the Atlantic Ocean were found to have a greater effect on the cod fish population than Greenland halibut which may have been attributed to the Atlantic cod's relatively pelagic niche where phytoplankton grow. Fish results may also be influenced by sampling anomalies, seasonal food web interactions, and genetic variances within the species.

5.6 References

(1) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated Flame Retardants in the Arctic Environment - Trends and New Candidates. *Sci. Total Environ.* **2010**, *408* (15), 2885–2918. https://doi.org/10.1016/j.scitotenv.2009.08.037.

(2) Chen, D.; Hale, R. C.; Letcher, R. J. Photochemical and Microbial Transformation of Emerging Flame Retardants: Cause for Concern? *Environ. Toxicol. Chem.* **2015**, *34* (4), 687–699. https://doi.org/10.1002/etc.2858.

(3) Haraguchi, K.; Ito, Y.; Takagi, M.; Fujii, Y.; Harada, K. H.; Koizumi, A. Levels, Profiles and Dietary Sources of Hydroxylated PCBs and Hydroxylated and Methoxylated PBDEs in Japanese Women Serum Samples. *Environ. Int.* **2016**, *97*, 155–162. https://doi.org/10.1016/j.envint.2016.08.022.

(4) Sarkar, A.; Knight, J. C.; Babichuk, N. A.; Mulay, S. Skewed Distribution of Hypothyroidism in the Coastal Communities of Newfoundland, Canada. *Environ. Int.* **2015**, *83*, 171–175. https://doi.org/10.1016/j.envint.2015.05.017.

(5) Wiseman, S. B.; Wan, Y.; Chang, H.; Zhang, X.; Hecker, M.; Jones, P. D.; Giesy, J. P. Polybrominated Diphenyl Ethers and Their Hydroxylated/Methoxylated Analogs: Environmental Sources, Metabolic Relationships, and Relative Toxicities. *6th Int. Conf. Mar. Pollut. Ecotoxicol.* **2011**, *63* (5–12), 179–188. https://doi.org/http://dx.doi.org/10.1016/j.marpolbul.2011.02.008.

(6) Shigematsu, H.; Ohta, S.; Shinohara, S.; Sugihara, K.; Uramaru, N.; Iwase, E.; Fujimoto, N.; Kitamura, S. Affinity for Thyroid Hormone and Estrogen Receptors of Hydroxylated Polybrominated Diphenyl Ethers. *J. Heal. Sci.* **2008**, *54* (5), 607–614. https://doi.org/10.1248/jhs.54.607.

(7) Dishaw, L. V; Macaulay, L. J.; Roberts, S. C.; Stapleton, H. M. Exposures, Mechanisms, and Impacts of Endocrine-Active Flame Retardants. *Curr. Opin. Pharmacol.* **2014**, *19* (117), 125–133. https://doi.org/10.1016/j.coph.2014.09.018.

(8) Zhang, K.; Wan, Y.; Giesy, J. P.; Lam, M. H. W.; Wiseman, S.; Jones, P. D.; Hu, J. Tissue Concentrations of Polybrominated Compounds in Chinese Sturgeon (Acipenser Sinensis): Origin, Hepatic Sequestration, and Maternal Transfer. *Environ. Sci. Technol.* **2010**, *44* (15), 5781–5786. https://doi.org/10.1021/es100348g.

(9) Kim, U.-J.; Jo, H.; Lee, I.-S.; Joo, G.-J.; Oh, J.-E. Investigation of Bioaccumulation and Biotransformation of Polybrominated Diphenyl Ethers, Hydroxylated and Methoxylated Derivatives in Varying Trophic Level Freshwater Fishes. *Chemosphere* **2015**, *137*, 108–114. https://doi.org/10.1016/j.chemosphere.2015.05.104.

(10) Teuten, E. L.; Xu, L.; Reddy, C. M. Two Abundant Bioaccumulated Halogenated Compounds Are Natural Products. *Science* **2005**, *307*, 917–920. https://doi.org/10.1126/science.1106882.

(11) Liu, Y.; Liu, J.; Yu, M.; Zhou, Q.; Jiang, G. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in a Marine Food Web of Chinese Bohai Sea and Their Human Dietary Exposure. *Environ. Pollut.* **2018**, *233*, 604–611. https://doi.org/10.1016/j.envpol.2017.10.105.

(12) Wen, Q.; Liu, H. ling; Zhu, Y. ting; Zheng, X. mei; Su, G. yong; Zhang, X. wei; Yu, H. xia; Giesy, J. P.; Lam, M. H. W. Maternal Transfer, Distribution, and Metabolism of BDE-47 and Its Related Hydroxylated, Methoxylated Analogs in Zebrafish (Danio Rerio). *Chemosphere* **2015**, *120*, 31–36. https://doi.org/10.1016/j.chemosphere.2014.05.050.

(13) Wan, Y.; Wiseman, S.; Chang, H.; Zhang, X.; Jones, P. D.; Hecker, M.; Kannan, K.; Tanabe, S.; Hu, J.; Lam, M. H. W. Origin of Hydroxylated Brominated Diphenyl Ethers: Natural Compounds or Man-Made Flame Retardants? *Environ. Sci. Technol.* **2009**, *43* (19), 7536–7542.

(14) Sharma, G. M.; Burkholder, P. R. Studies on the Antimicrobial Substances of Sponges II. Structure and Synthesis of a Bromine-Containing Antibacterial, Compound from a Marine Sponge. *Tetrahedron Lett.* **1967**, *8* (42), 4147–4150. https://doi.org/10.1016/S0040-4039(01)89710-0.

(15) Carté, B.; Faulkner, D. J. Polybrominated Diphenyl Ethers from Dysidea Herbacea, Dysidea Chlorea and Phyllospongia Foliascens. *Tetrahedron* **1981**, *37* (13), 2335–2339. https://doi.org/10.1016/S0040-4020(01)88886-4.

(16) Schorn, M. A.; Jordan, P. A.; Podell, S.; Blanton, J. M.; Agarwal, V.; Biggs, J. S.; Allen, E. E.; Moorea, B. S. Comparative Genomics of Cyanobacterial Symbionts Reveals Distinct, Specialized Metabolism in Tropical Dysideidae Sponges. *Am. Soc. Microbiol.* **2019**, *10* (3), 1–15.

(17) Schorn, M. A.; Jordan, P. A.; Podell, S.; Blanton, J. M.; Agarwal, V.; Biggs, J. S.; Allen, E. E.; Moore, B. S. Comparative Genomics of Cyanobacterial Symbionts Reveals Distinct, Specialized Metabolism in Tropical <Em>Dysideidae</Em> Sponges. *MBio* **2019**, *10* (3), e00821-19. https://doi.org/10.1128/mBio.00821-19.

(18) Zhang, K.; Wan, Y.; Jones, P. D.; Wiseman, S.; Giesy, J. P.; Hu, J. Occurrences and Fates of Hydroxylated Polybrominated Diphenyl Ethers in Marine Sediments in Relation to Trophodynamics. *Environ. Sci. Technol.* **2012**, *46* (4), 2148–2155. https://doi.org/10.1021/es203195s.

(19) Sun, J.; Liu, J.; Liu, Y.; Jiang, G. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in Mollusks from Chinese Coastal Areas. *Chemosphere* **2013**, *92* (3), 322–328. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2013.03.042.

(20) Mizukawa, K.; Yamada, T.; Matsuo, H.; Takeuchi, I.; Tsuchiya, K.; Takada, H. Biomagnification and Debromination of Polybrominated Diphenyl Ethers in a Coastal Ecosystem in Tokyo Bay. *Sci. Total Environ.* **2013**, *449*, 401–409. https://doi.org/10.1016/j.scitotenv.2013.01.092.

(21) OSPAR. *CEMP Guidelines for Monitoring Contaminants in Biota (Agreement 1999-02).*; London, UK., 1999.

(22) Wu, Y.; Tan, H.; Zhou, C.; Crimmins, B. S.; Holsen, T. M.; Pagano, J. J.; Chen, D. Spatial and Temporal Trends (2004 – 2016) of Selected Alternative Flame Retardants in Fish of the Laurentian Great Lakes. *Environ. Sci. Technol.* **2019**, *53* (4), 1786–1796. https://doi.org/10.1021/acs.est.8b05300.

(23) Boitsov, S.; Grøsvik, B. E.; Nesje, G.; Malde, K.; Klungsøyr, J. Levels and Temporal Trends of Persistent Organic Pollutants (POPs) in Atlantic Cod (Gadus Morhua) and Haddock (Melanogrammus Aeglefinus) from the Southern Barents Sea. *Environ. Res.* **2019**, *172*, 89–97. https://doi.org/10.1016/j.envres.2019.02.008.

(24) Löfstrand, K.; Malmvärn, A.; Haglund, P.; Bignert, A.; Bergman, Å.; Asplund, L. Brominated Phenols, Anisoles, and Dioxins Present in Blue Mussels from the Swedish Coastline. *Environ. Sci. Pollut. Res.* **2010**, *17* (8), 1460–1468. https://doi.org/10.1007/s11356-010-0331-1.

(25) Dennard, S. T.; McMeans, B. C.; Fisk, A. T. Preliminary Assessment of Greenland Halibut Diet in Cumberland Sound Using Stable Isotopes. *Polar Biol.* **2009**, *32* (6), 941–945. https://doi.org/10.1007/s00300-009-0624-3.

(26) Wolkers, H.; Lydersen, C.; Kovacs, K. M.; Burkow, I.; Bavel, B. Van. Accumulation, Metabolism, and Food-Chain Transfer of Chlorinated and Brominated Contaminants in Subadult White Whales (Delphinapterus Leucas) and Narwhals (Monodon Monoceros) From Svalbard, Norway. **2006**, *78*, 69–78. https://doi.org/10.1007/s00244-004-0257-z.

(27) Lear, W. H.; Green, J. M. Migration of the “Northern” Atlantic Cod and the Mechanisms Involved. In *Mechanisms of Migration in Fishes*; McCleave J.D., Arnold G.P., Dodson J.J., N. W. H., Ed.; Mechanisms of Migration in Fishes. NATO Conference Series (IV Marine Sciences): Springer, Boston, MA, 1984; Vol. 14, pp 309–315. https://doi.org/10.1007/978-1-4613-2763-9_19.

(28) O'Brien, L.; Burnett, J.; Mayo, R. K. Maturation of Nineteen Species of Finfish off the Northeast Coast of the United States, 1985-1990. *NOAA Tech. Rep.* **1993**, *NMFS 113* (June), 66 p.

(29) Nøstbakken, O. J.; Duinker, A.; Rasinger, J. D.; Nilsen, B. M.; Sanden, M.; Frantzen, S.; Hove, H. T.; Lundebye, A. K.; Berntssen, M. H. G.; Hannisdal, R.; et al. Factors Influencing Risk Assessments of Brominated Flame-Retardants; Evidence Based on Seafood from the North East Atlantic Ocean. *Environ. Int.* **2018**, *119* (December 2017), 544–557. https://doi.org/10.1016/j.envint.2018.04.044.

(30) Bustnes, J. O.; Borgå, K.; Dempster, T.; Lie, E.; Nygård, T.; Uglem, I. Latitudinal Distribution of Persistent Organic Pollutants in Pelagic and Demersal Marine Fish on the Norwegian Coast. *Environ. Sci. Technol.* **2012**, *46* (14), 7836–7843.

(31) Salvadó, J. A.; Grimalt, J. O.; López, J. F.; Durrieu De Madron, X.; Heussner, S.; Canals, M. Transformation of PBDE Mixtures during Sediment Transport and Resuspension in Marine Environments (Gulf of Lion, NW Mediterranean Sea). *Environ. Pollut.* **2012**, *168*, 87–95. https://doi.org/10.1016/j.envpol.2012.04.019.

(32) Kelly, B. C.; Blair, J. D.; Gobas, F. A. P. C.; Ikonomou, M. G. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers in a Canadian Arctic Marine Food Web. *Environ. Sci. Technol.* **2008**, *42* (19), 7069–7077. https://doi.org/10.1021/es801275d.

(33) Sühring, R.; Busch, F.; Fricke, N.; Kötke, D.; Wolschke, H.; Ebinghaus, R. Science of the Total Environment Distribution of Brominated Flame Retardants and Dechloranes between Sediments and Benthic Fish — A Comparison of a Freshwater and Marine Habitat. *Sci. Total Environ.* **2016**, *542*, 578–585. https://doi.org/10.1016/j.scitotenv.2015.10.085.

(34) Haglund, P. S.; Zook, D. R.; Buser, H. R.; Hu, J. Identification and Quantification of Polybrominated Diphenyl Ethers and Methoxy-Polybrominated Diphenyl Ethers in Baltic Biota. *Environ. Sci. Technol.* **1998**, *31* (11), 3281–3287. https://doi.org/10.1039/b412924p.

(35) Hung, H.; Katsoyiannis, A. A.; Brorström-Lundén, E.; Olafsdottir, K.; Aas, W.; Breivik, K.; Bohlin-Nizzetto, P.; Sigurdsson, A.; Hakola, H.; Bossi, R.; et al. Temporal Trends of Persistent Organic Pollutants (POPs) in Arctic Air: 20 Years of Monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.* **2016**, *217*, 52–61. https://doi.org/10.1016/j.envpol.2016.01.079.

(36) W.A. Johnston, F.J. Nicholson, A. R. and G. D. S. *FAO FISHERIES TECHNICAL PAPER - 340*; FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS: Torry, Aberdeen, Scotland, UK, 1994. https://doi.org/M-47.

(37) Falandysz, J.; Smith, F.; Steel, Z.; Fernandes, A. R. PBDEs in Cod (Gadus Morhua) Liver Products (1972 to 2017): Occurrence and Human Exposure. *Chemosphere* **2019**, *232*, 63–69. https://doi.org/10.1016/j.chemosphere.2019.05.139.

(38) Bakke, T.; Boitsov, S.; Brevik, E. M.; Gabrielsen, G. W.; Green, N.; Helgason, L. B.; Klungsøyr, J.; Leknes, H.; Miljeteig, C.; Måge, A.; Rolfsnes, B. E.; Savinova, T.; Schlabach, M.; Skaare, B. B.; Valdersnes, S. *Mapping Selected Organic Contaminants in The*; Norwegian Pollution Control Authority: Oslo, Norway, 2008.

(39) Roszko, M.; Szymczyk, K.; Rzepkowska, M.; Jędrzejczak, R. Preliminary Study on Brominated Dioxins/Furans and Hydroxylated/Methoxylated PBDEs in Baltic Cod (Gadus Morhua) Liver. Comparison to the Levels of Analogue Chlorinated Co-Occurring Pollutants. *Mar. Pollut. Bull.* **2015**, *96* (1–2), 165–175. https://doi.org/10.1016/j.marpolbul.2015.05.032.

(40) Houde, M.; Berryman, D.; Lafontaine, Y. De; Verreault, J. Science of the Total Environment Novel Brominated Flame Retardants and Dechloranes in Three Fish Species from the St. Lawrence River , Canada. *Sci. Total Environ.* **2014**, *479–480*, 48–56. https://doi.org/10.1016/j.scitotenv.2014.01.105.

(41) Julshamn, K.; Duinker, A.; Berntssen, M.; Nilsen, B. M.; Frantzen, S.; Nedreaas, K.; Maage, A. A Baseline Study on Levels of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, Non-Ortho and Mono-Ortho PCBs, Non-Dioxin-like PCBs and Polybrominated Diphenyl Ethers in Northeast Arctic Cod (Gadus Morhua) from Different Parts of the Baren. *Mar. Pollut. Bull.* **2013**, *75* (1–2), 250–258. https://doi.org/10.1016/j.marpolbul.2013.07.017.

(42) Héloïse Frouin, Michel Lebeuf, Mike Hammill, Becky Sjare, M. F. PBDEs in Serum and Blubber of Harbor, Grey and Harp Seal Pups from Eastern Canada. *Chemosphere* **2010**, *82* (5), 663–669. https://doi.org/10.1016/j.chemosphere.2010.11.007.

(43) Gregg T. Tomy, Kerri Pleskach, Tyler Oswald, Thor Halldorson, Paul A. Helm, Gordia MaCinnis, and C. H. M. Enantioselective Bioaccumulation of Hexabromocyclododecane and Congener-Specific Accumulation of Brominated Diphenyl Ethers in an Eastern Canadian Arctic Marine Food Web. **2008**, *42* (10), 3634–3639.

(44) Haglund, P.; Löfstrand, K.; Malmvärn, A.; Bignert, A.; Asplund, L. Temporal Variations of Polybrominated Dibenzo-p-Dioxin and Methoxylated Diphenyl Ether Concentrations in Fish Revealing Large Differences in Exposure and Metabolic Stability. *Environ. Sci. Technol.* **2010**, *44* (7), 2466–2473. https://doi.org/10.1021/es9038006.

(45) Sinkkonen, S.; Rantalainen, A.-L.; Paasivirta, J.; Lahtiperä, M. Polybrominated Methoxy Diphenyl Ethers (MeO-PBDEs) in Fish and Guillemot of Baltic, Atlantic and Arctic Environments. *Chemosphere* **2004**, *56* (8), 767–775. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2004.02.007.

(46) Choo, G.; Kim, D.-H.; Kim, U.-J.; Lee, I.-S.; Oh, J.-E. PBDEs and Their Structural Analogues in Marine Environments: Fate and Expected Formation Mechanisms Compared with Diverse Environments. *J. Hazard. Mater.* **2018**, *343*, 116–124. https://doi.org/10.1016/j.jhazmat.2017.09.026.

(47) Löfstrand, K.; Liu, X.; Lindqvist, D.; Jensen, S.; Asplund, L. Seasonal Variations of Hydroxylated and Methoxylated Brominated Diphenyl Ethers in Blue Mussels from the Baltic Sea. *Chemosphere* **2011**, *84* (4), 527–532. https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2011.01.001.

(48) Dillon Consulting Limited. Study of Options for Organic Waste Processing in the Province of Newfoundland and Labrador. **2014**.

(49) NASA Goddard Space Flight Center, O. B. P. G. Sea-viewing Wide Field-of-view Sensor (SeaWiFS) Ocean Color Data. https://doi.org/data/10.5067/AQUA/MODIS/L3M/CHL/2018.

(50) Malmvärn, A.; Zebühr, Y.; Kautsky, L.; Bergman, Å.˚; Asplund, L. Hydroxylated and Methoxylated Polybrominated Diphenyl Ethers and Polybrominated Dibenzo-p-Dioxins in Red Alga and Cyanobacteria Living in the Baltic Sea. *Chemosphere* **2008**, *72* (6), 910–916. https://doi.org/10.1016/j.chemosphere.2008.03.036.

(51) Wang, Y.; Wu, X.; Zhao, H.; Xie, Q.; Hou, M.; Zhang, Q.; Du, J.; Chen, J. Characterization of PBDEs and Novel Brominated Flame Retardants in Seawater near a Coastal Mariculture Area of the Bohai Sea, China. *Sci. Total Environ.* **2017**, *580*, 1446–1452. https://doi.org/10.1016/j.scitotenv.2016.12.114.

(52) Sørmo EG, Jenssen BM, Lie E, S. J. Brominated Flame Retardants in Aquatic Organisms from the North Sea in Comparison with Biota from the High Arctic Marine Environment. *Env. Toxicol Chem* **2009**, No. 28, 2082–2090.

(53) Söderström, G.; Sellström, U.; De Wit, C. A.; Tysklind, M. Photolytic Debromination of Decabromodiphenyl Ether (BDE 209). *Environ. Sci. Technol.* **2004**, *38* (1), 127–132. https://doi.org/10.1021/es034682c.

(54) Jianxian, S.; Hui, P.; Jianying, H. Temporal Trends of Polychlorinated Biphenyls, Polybrominated Diphenyl Ethers, and Perfluorinated Compounds in Chinese Sturgeon (*Acipenser Sinensis*) Eggs (1984–2008). *Environ. Sci. Technol.* **2015**, *49* (3), 1621–1630. https://doi.org/10.1021/es505378b.

(55) Eriksson, J.; Green, N.; Marsh, G.; Bergman, Å.̊. Photochemical Decomposition of 15 Polybrominated Diphenyl Ether Congeners in Methanol/Water. *Environ. Sci. Technol.* **2004**, *38* (11), 3119–3125. https://doi.org/10.1021/es049830t.

(56) Jacobs, M. N.; Covaci, A.; Gheorghe, A.; Schepens, P. Time Trend Investigation of PCBs, PBDEs, and Organochlorine Pesticides in Selected n-3 Polyunsaturated Fatty Acid Rich Dietary Fish Oil and Vegetable Oil Supplements; Nutritional Relevance for Human Essential n-3 Fatty Acid Requirements. *J. Agric. Food Chem.* **2004**, *52* (6), 1780–1788. https://doi.org/10.1021/jf035310q.

(57) Rotander, A.; van Bavel, B.; Rigét, F.; Auðunsson, G. A.; Polder, A.; Gabrielsen, G. W.; Víkingsson, G.; Mikkelsen, B.; Dam, M.; AuDunsson, G. A.; et al. Methoxylated Polybrominated Diphenyl Ethers (MeO-PBDEs) Are Major Contributors to the Persistent Organobromine Load in Sub-Arctic and Arctic Marine Mammals, 1986–2009. *Sci. Total Environ.* **2012**, *416*, 482–489. https://doi.org/10.1016/j.scitotenv.2011.12.010.

(58) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011**, *45* (5), 1820–1826. https://doi.org/10.1021/es103803t.

(59) Li, J.; Li, Q.; Gioia, R.; Zhang, Y.; Zhang, G.; Li, X.; Spiro, B.; Bhatia, R. S.; Jones, K. C. PBDEs in the Atmosphere over the Asian Marginal Seas, and the Indian and Atlantic Oceans. *Atmos. Environ.* **2011**, *45* (37), 6622–6628. https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2011.09.010.

(60) Alonso, M. B.; Azevedo, A.; Torres, J. P. M.; Dorneles, P. R.; Eljarrat, E.; Barceló, D.; Lailson-Brito, J.; Malm, O. Anthropogenic (PBDE) and Naturally-Produced (MeO-PBDE) Brominated Compounds in Cetaceans - A Review. *Sci. Total Environ.* **2014**, *481* (1), 619–634. https://doi.org/10.1016/j.scitotenv.2014.02.022.

(61) Gillis, M. What's in Your Harbour? Scientist Appalled by Newfoundland's Underwater Trash Problem. *CBC News*. St. John's, Newfoundland November 22, 2017.

(62) Van Ael, E.; Covaci, A.; Blust, R.; Bervoets, L. Persistent Organic Pollutants in the Scheldt Estuary: Environmental Distribution and Bioaccumulation. *Environ. Int.* **2012**, *48*, 17–27. https://doi.org/10.1016/j.envint.2012.06.017.

(63) Dabrowska, H.; Kopko, O.; Lehtonen, K. K.; Lang, T.; Waszak, I.; Balode, M.; Strode, E. An Integrated Assessment of Pollution and Biological Effects in Flounder, Mussels and Sediment in the Southern Baltic Sea Coastal Area. *Environ. Sci. Pollut. Res.* **2016**, *24* (4), 3626–3639. https://doi.org/10.1007/s11356-016-8117-8.

(64) Law, R. J.; Alaee, M.; Allchin, C. R.; Boon, J. P.; Lebeuf, M.; Lepom, P.; Stern, G. A. Levels and Trends of Polybrominated Diphenylethers and Other Brominated Flame Retardants in Wildlife. *State-of-Science Trends BFRs Environ.* **2003**, *29* (6), 757–770. https://doi.org/http://dx.doi.org/10.1016/S0160-4120(03)00110-7.

(65) Frampton, P. C. B.; Scruton, D. A.; Cote, D.; McKinley, R. S.; Moulton, S. Habitat Use and Early Winter Movements by Juvenile Atlantic Cod in a Coastal Area of Newfoundland. *J. Fish Biol.* **2004**, *64* (3), 665–679. https://doi.org/10.1111/j.1095-8649.2004.00331.x.

6. Conclusions and future directions

6.1 Conclusions

Aerosol mechanisms may link marine polybrominated diphenyl ethers (PBDEs) and their natural methoxy analogues (MeO-BDEs) pools to the atmosphere, globally influencing the general biosphere as they long range transport (LRT) on aerosols. The micro orifice uniform deposition impactor (MOUDI) have collected aerodynamic aerosol samples to determine PBDE and MeO-BDE sources and increased their potential for LRT. Duration of atmospheric collections were increased (one month) and the sampling site was relocated to compensate for the relatively low aerosol abundance and PBDE levels associated with of Newfoundland and Labrador (NL). Atlantic cod and Greenland halibut fish, a staple NL fisheries and traditional diet, were analyzed of their livers to characterize PBDEs and MeO-BDEs with respect to their sampled origins in the Gulf of the St. Lawrence and the Atlantic Ocean.

Extraction and analysis of PBDEs and MeO-BDEs from complex environmental matrices is essential to understanding their environmental fate. In Chapter 2, it was demonstrated the effective replacement of the commonly used dichloromethane (DCM) extraction solvent with a less environmentally harmful and more efficient hexane:toluene (9:1) solvent mix. An automated accelerate solvent extraction (ASE) setup along with this extraction solvent improved the efficiency of the manual extraction technique. The GC temperature program and general instrument maintenance were adjusted to accommodate the many samples analyzed and the evaluation of numerous PBDE analytes in each sample run.

Accurate calibration of PBDEs and MeO-BDEs is also necessary for effective quantification. In Chapter 3, it was described an assessment of sample matrices (standard reference material (SRM) 2585 household dust and cod fish liver) with standard addition, internal standard, and external standard calibrations of the targeted PBDEs that were used to evaluate an internal standard appropriate for this study. The use of FBDE-69 as the universal internal standard for PBDE analysis has drawn criticism for its fluoro-group resolving the compound earlier than all the PBDEs, thus not likely experiencing the same matrix effects. When compared to the true values produced from the standard addition analysis, the accuracy of FBDE-69 was poorer than the accuracy achieved by the external standard calibration. According to this study, BDE-118 accurately measured the most important environmental PBDE (BDE-47) and natural MeO-BDE (congeners 6-MeO-BDE-47 and 2'-MeO-BDE-68), therefore became the most appropriate internal standard for this study.

Using the methods developed in Chapters 2 and 3, it was measured size-resolved aerosol PBDE and MeO-BDE composition in St. John's, NL. In Chapter 4, it was demonstrated that overall PBDE and MeO-BDE loadings onto fine and ultrafine aerosol modes were indicative of atmospheric LRT potential. Although other studies have established temperature-dependent partitioning of persistent organic pollutants (POPs) onto aerosols, associated environmental parameters of wind speed and temperature that may influence aerosol production were not consistent with the former, but moderately

affected by the latter in these results. Alternatively, these PBDE levels may be a product of local indoor-outdoor air exchange or from global air masses.

These developed methods were also used to examine fish from the Atlantic Ocean collected around the island of Newfoundland, as described in Chapter 5. The international ban on PBDE manufacturing and the remediation of NL landfills to reduce organics and subsequently reduce phytoplankton primary production associated with landfill runoff could be responsible for the relatively lower analyte levels in 2014 fish samples compared to 1993 samples. Ocean depth profiles generally showed no correlation with analyte concentrations. Greenland halibut showed a significant trend with PBDEs and oceanic depth that may be attributed to the sediment layer that is known to harbor larger PBDE congeners. However, this depth trend may have been driven by a single outlier. PBDE and MeO-BDE were found to be greater in the Gulf of St. Lawrence than the Atlantic Ocean that could indicate dilution effects. According to the relatively higher MeO-BDE concentrations in Greenland halibut, MeO-BDE producing phytoplankton common in the pelagic ocean may be a greater influence in this fish's life cycle. Overall, cod fish livers consisted of greater PBDEs than Greenland halibut. Although cod fish are categorized as benthic fish, their life cycle consists of a greater proportion in the open water than Greenland halibut, thus may be more exposed to PBDE atmospheric deposition as well as MeO-BDE from phytoplankton.

6.2 Future directions

This work raises additional questions that could be addressed in future studies. Future work to determine these aerosol patterns and sources could include stationed aerosol collection throughout the coastal and inland regions of NL and other northern regions over a course of a few years to produce a seasonal aerosol loading gradient. Considering that MOUDI samples are a sample set of N = 1 for a given collection term, numerous MOUDI samplers could be used in one region or one MOUDI setup could be arranged with other aerosol denuders to improve statistical samples size while keeping operating costs to a minimum. Upcoming aerosol technologies and mapping software may also be used to improve this analysis and to smoothly moderate operations between sampling systems.

Future marine and food web assessments would consist of extending this food web analysis to the prey fish (capelin) and the predators (whales, seals, humans) that consume these Atlantic fish. Sediment, water, and microsurface layer should also be included in future analysis. Further study in new fire retardants and their replacements could give further insight in POP LRT and their sources.

Appendix A Supporting Information for Chapter 3

Table A-1. Internal standard calibration curve: 200 µL total volume.

Concentration (µg/L)	0	1	2.5	5	15	25
Wellington Standard BDE-MX	0 µL	2 µL (100 µg/L)	4 µL (100 µg/L)	10 µL (100 µg/L)	5 µL (500 µg/L)	40 µL (500 µg/L)
MeO-BDE-MX (50 ppb)	0 µL	4 µL	8 µL	20 µL	50 µL	100 µL
Toluene	200 µL	198 µL	196 µL	180 µL	150 µL	100 µL
Internal Standard BDE-118 (2 ppm)	10 µL	10 µL	10 µL	10 µL	10 µL	10 µL

Table A-2. Standard addition calibration curve: 240 µL total volume.

Concentration (µg/L)	0	1	2.5	5	15	25
SRM Dust/Fish	200 µL	200 µL	200 µL	200 µL	200 µL	200 µL
Wellington Standard BDE-MX	0 µL	2 µL (Stock 100 µg/L)	4 µL (100 µg/L)	2 µL (Stock 500 µg/L)	5 µL (500 µg/L)	40 µL (500 µg/L)
MeO-BDE-MX (1 ppm)	0 µL	0.25 µL	0.625 µL	1.25 µL	3.75 µL	6.25 µL
Toluene	50 µL	47.75 µL	45.375 µL	46.75 µL	41.25 µL	3.75 µL

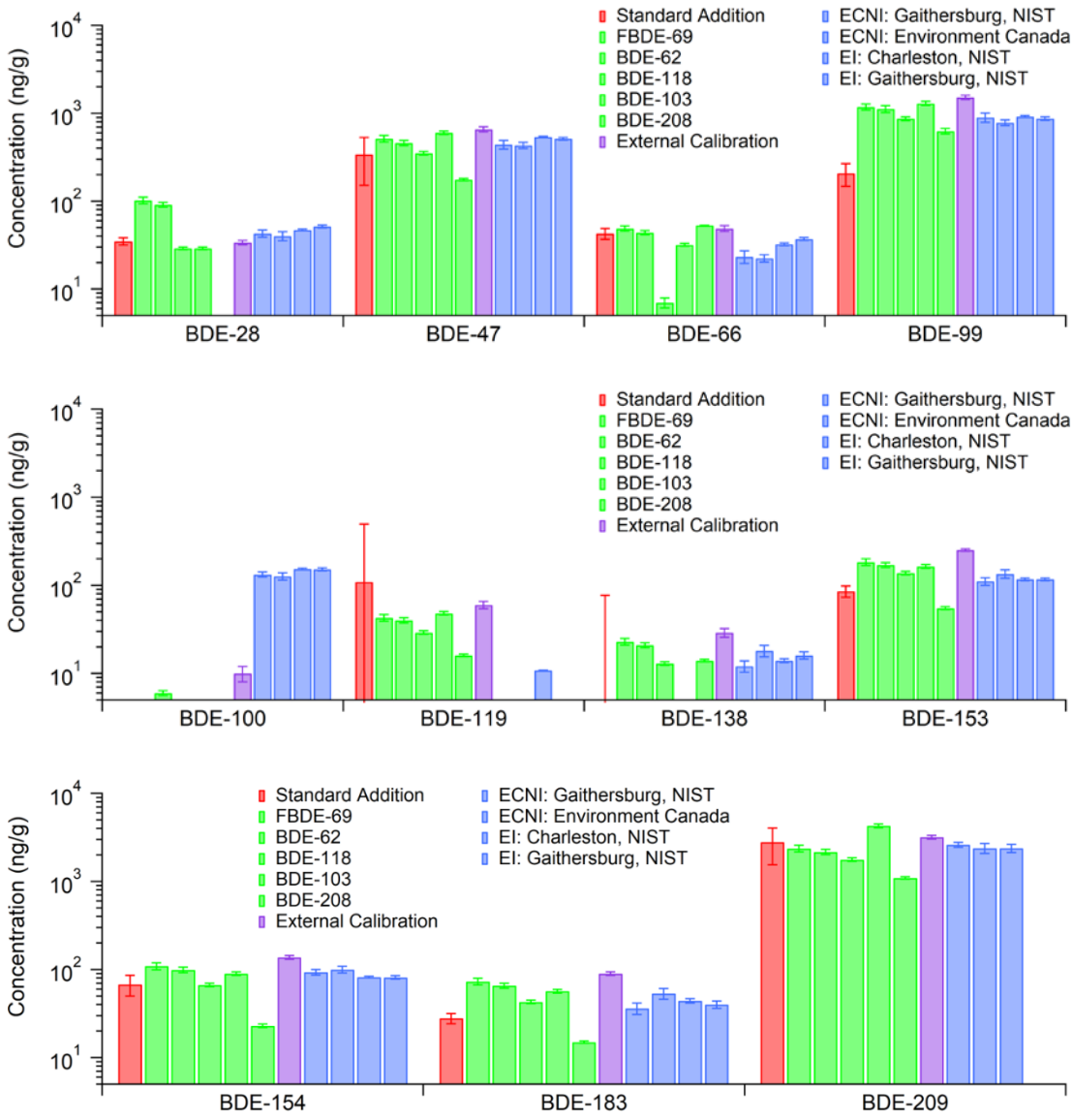

Figure A-1. 2585 SRM house dust standard addition, internal standard calibration, external standard calibration, and literature comparison. Internal standards and reported data are reported in the order they are listed in the legend.

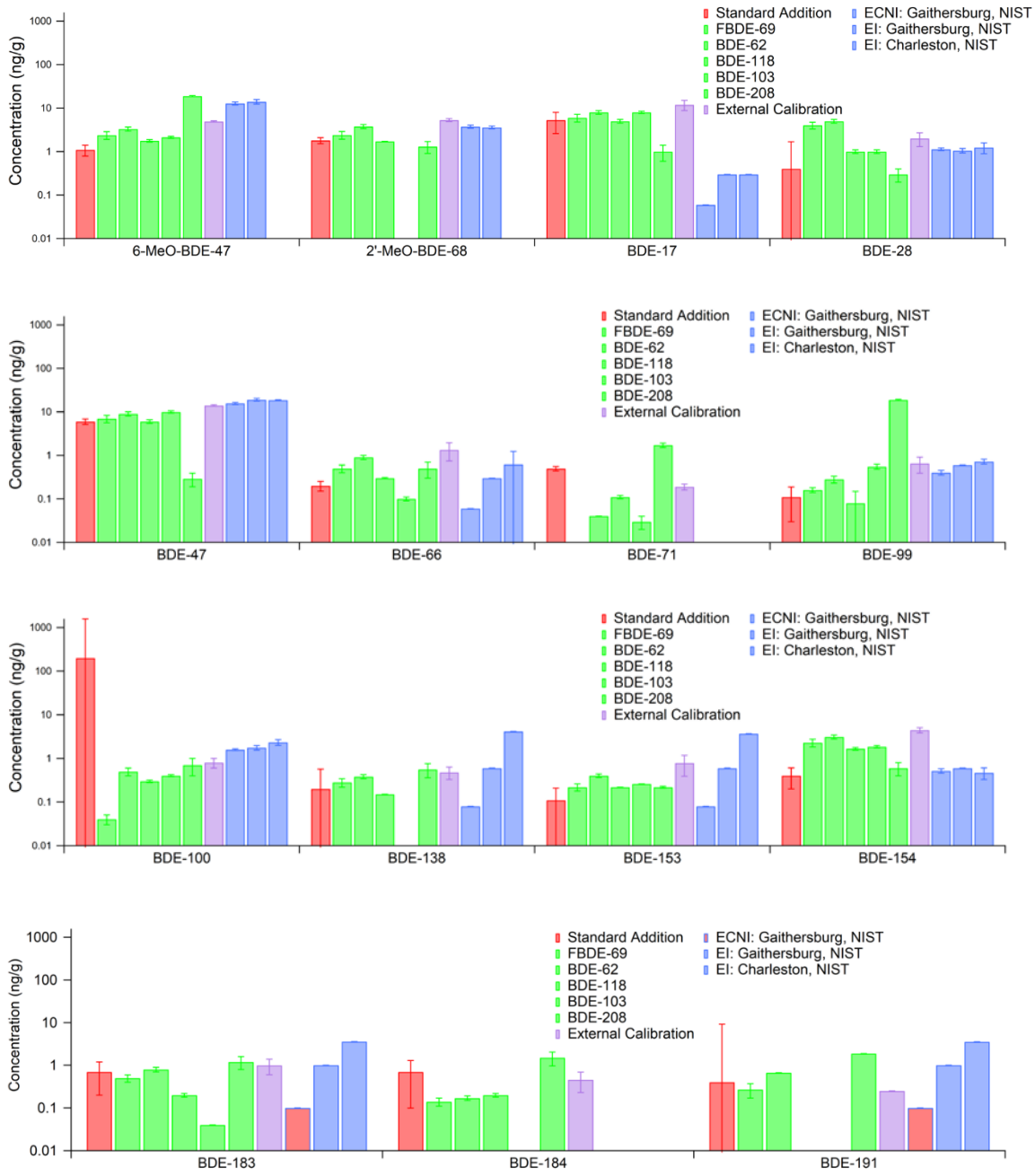

Figure A-2. Atlantic cod fish liver standard addition, internal standard calibration, external standard calibration, and literature comparison. Internal standards and reported data are reported in the order they are listed in the legend.

Appendix B. Supporting Information for Chapter 4

Equation B-1. Calculation of $dm/dlogd_p$ (d_p, particle size). Final units of $dm/dlogd_p$ in pg/m^3. Units for each quantity as follows: d_p (µm), m (pg), sampling rate (m^3/h), sampling time (h).

$$\frac{dm}{dlogd_p} = \frac{2.303 \times median\ d_p \times m_{total,analyte}}{\frac{sampling\ rate \times sampling\ time}{range\ d_p}}$$

Table B-1. Sampling stage particle sizes for MOUDI sampler used in this study.

Stage	Cut size (µm)	Median (µm)	Range (µm)
0	32	25	14
1	18	14	8
2	10	7.8	4.4
3	5.6	4.4	2.4
4	3.2	2.5	1.4
5	1.8	1.4	0.8
6	1	0.78	0.44
7	0.56	0.44	0.24
8	0.32	0.25	0.14
9	0.18	0.14	0.08
10	0.1	0.078	0.044
11	0.056	0.044	0.024
12	0.032	0.025	0.014
13	0.018	0.014	0.008

B.1 MOUDI analysis method detection limit

A gas chromatography mass spectroscopy (GC-MS) run of ~27 min per sample (including automated solvent syringe cleaning and sample transfer) for a continuous GC-MS analysis of about 20 to 100 samples, including solvent blanks and internal standard calibration, could operate for a few hours to about a day. The sample method detection limit (Table B-1) was calculated with a field blank 10 seconds at the beginning of each MOUDI sampling. Field blanks were immediately stored in a petri dish and stored at -18^{o}C. All MOUDI samples and field blanks were randomly quantified with 3 different calibration curves to prevent systematic bias and monitor instrumental stability during these long GC-MS runs.

Table B-2. Method detection limit (MDL, ng) of MOUDI aerosol samples.

Sample Start Date	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-BDE-68	6-MeO-BDE-47
July 28 2015	0.548	0.197	0.058	0.00	0.152	0.020
Aug. 24, 2015	0.328	0.134	0.035	0.00	0.045	0.00
Jan. 27, 2016	0.312	0.278	0.206	0.00	0.038	0.045
May 31, 2016	0.398	0.108	0.037	0.000	0.025	0.000
June 30, 2016	1.168	0.377	0.088	0.147	0.248	0.000
Aug. 2, 2016	0.920	0.426	0.112	0.000	0.189	0.000
Sept. 9, 2016	0.547	0.216	0.039	0.00	0.104	0.000

Table B-3. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (July 28, 2015 to August 24, 2015).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	0.017	0.124	0.038	<MDL	0.016	<MDL
M1	<MDL	0.083	0.094	<MDL	<MDL	<MDL
M2	<MDL	0.040	0.086	<MDL	<MDL	<MDL
M3	0.472	0.414	0.160	<MDL	0.280	<MDL
M4	<MDL	<MDL	0.012	<MDL	<MDL	<MDL
M5	<MDL	0.123	0.096	<MDL	<MDL	<MDL
M6	<MDL	0.174	0.160	<MDL	<MDL	<MDL
M7	0.273	0.241	0.055	<MDL	0.052	<MDL
M8	<MDL	0.414	0.374	<MDL	<MDL	<MDL
M9	<MDL	<MDL	0.014	<MDL	<MDL	<MDL
M10	0.896	0.459	0.214	<MDL	0.621	<MDL
M11	1.650	0.560	0.193	23.60	<MDL	<MDL
M12	0.884	0.321	0.157	<MDL	<MDL	<MDL
M13	<MDL	0.155	0.136	<MDL	<MDL	<MDL

MDL = Method detection limit

Table B-4. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (August 24, 2015 to October 8, 2015).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	<MDL	0.0184	<MDL	<MDL	<MDL	<MDL
M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M2	<MDL	0.0446	0.0467	<MDL	0.0295	<MDL
M3	0.4749	0.1783	0.0550	<MDL	0.0171	<MDL
M4	0.0181	0.0229	0.0294	<MDL	0.0347	<MDL
M5	<MDL	<MDL	0.0309	<MDL	0.0097	<MDL
M6	<MDL	<MDL	0.0019	<MDL	<MDL	<MDL
M7	<MDL	0.0281	0.1455	<MDL	0.0487	<MDL
M8	<MDL	<MDL	0.0342	<MDL	0.0404	<MDL
M9	<MDL	0.0087	0.0066	<MDL	0.0211	<MDL
M10	0.9390	0.3155	0.1311	<MDL	0.1615	<MDL
M11	<MDL	0.1554	0.2942	23.60	0.0661	<MDL
M12	<MDL	0.0377	0.0710	<MDL	<MDL	<MDL
M13	<MDL	0.0275	0.2340	<MDL	<MDL	<MDL

MDL = Method detection limit

Table B-5. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (January 27, 2016 to February 29, 2016).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M5	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M6	0.4656	<MDL	<MDL	<MDL	<MDL	<MDL
M7	<MDL	<MDL	<MDL	<MDL	0.0654	<MDL
M8	0.5859	<MDL	<MDL	<MDL	<MDL	<MDL
M9	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M10	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M11	<MDL	<MDL	<MDL	<MDL	0.1400	<MDL
M12	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

MDL = Method detection limit

Table B-6. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (May 31, 2016 to June 29, 2016).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	0.4540	<MDL	0.0138	<MDL	0.0570	<MDL
M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M2	0.7707	0.2121	0.0421	<MDL	<MDL	<MDL
M3	0.3859	<MDL	0.0639	0.4744	<MDL	<MDL
M4	<MDL	<MDL	<MDL	0.3077	<MDL	<MDL
M5	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M6	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M7	0.1837	<MDL	<MDL	<MDL	<MDL	<MDL
M8	<MDL	0.2371	<MDL	<MDL	<MDL	<MDL
M9	0.2311	0.5172	0.4345	0.2502	0.1500	<MDL
M10	0.2333	<MDL	<MDL	<MDL	<MDL	<MDL
M11	0.2425	0.9446	0.8297	<MDL	0.0634	<MDL
M12	<MDL	0.2498	<MDL	<MDL	<MDL	<MDL
M13	<MDL	<MDL	<MDL	<MDL	0.0327	<MDL

MDL = Method detection limit

Table B-7. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (June 30, 2016 to August 1, 2016).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	<MDL	<MDL	0.1323	0.6767	<MDL	<MDL
M1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M2	<MDL	<MDL	0.0882	2.9682	<MDL	<MDL
M3	0.9319	0.2226	<MDL	<MDL	<MDL	<MDL
M4	<MDL	0.7620	2.2112	<MDL	<MDL	0.3641
M5	<MDL	0.4112	0.2942	0.9924	<MDL	<MDL
M6	<MDL	0.1334	0.2092	<MDL	<MDL	<MDL
M7	<MDL	<MDL	0.0696	<MDL	<MDL	<MDL
M8	1.1432	0.5634	0.2110	<MDL	0.2163	<MDL
M9	<MDL	0.5794	0.3928	0.9152	<MDL	<MDL
M10	<MDL	0.4281	0.4663	<MDL	<MDL	<MDL
M11	0.4343	0.3617	0.4942	1.2212	<MDL	<MDL
M12	<MDL	0.0454	<MDL	<MDL	<MDL	<MDL
M13	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

MDL = Method detection limit

Table B-8. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (August 2, 2016 to September 7, 2016).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	<MDL	<MDL	0.0137	0.2496	<MDL	<MDL
M1	<MDL	<MDL	<MDL	0.2818	<MDL	<MDL
M2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M3	<MDL	<MDL	0.0449	<MDL	<MDL	<MDL
M4	<MDL	<MDL	0.0962	<MDL	<MDL	<MDL
M5	<MDL	<MDL	0.0708	<MDL	<MDL	<MDL
M6	<MDL	0.0376	0.1962	<MDL	0.0201	<MDL
M7	<MDL	<MDL	<MDL	0.4466	<MDL	<MDL
M8	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
M9	<MDL	<MDL	0.0870	<MDL	<MDL	<MDL
M10	<MDL	<MDL	0.1640	<MDL	<MDL	<MDL
M11	<MDL	<MDL	0.4727	0.4427	0.2052	<MDL
M12	<MDL	<MDL	0.0973	<MDL	0.0214	<MDL
M13	<MDL	<MDL	<MDL	0.3540	<MDL	<MDL

MDL = Method detection limit

Table B-9. MOUDI aerosol $dM/dlogd_P$ (pg/m^3) sample collection (September 9, 2016 to October 7, 2016).

Stage	BDE-28	BDE-47	BDE-99	BDE-209	2'-MeO-68	6-MeO-47
M0	0.3685	0.2460	0.3232	<MDL	<MDL	0.1554
M1	1.9876	0.2692	0.0677	<MDL	<MDL	0.0463
M2	<MDL	0.2216	0.1307	<MDL	<MDL	0.1261
M3	<MDL	0.0743	0.0949	<MDL	<MDL	0.0684
M4	<MDL	0.0926	0.0582	<MDL	0.0212	0.0362
M5	<MDL	0.3760	0.4011	<MDL	<MDL	0.1840
M6	<MDL	0.2359	0.1557	<MDL	0.0086	0.0927
M7	<MDL	<MDL	0.1068	<MDL	<MDL	0.0768
M8	1.5120	0.4785	0.1461	<MDL	<MDL	0.1218
M9	<MDL	0.1510	0.1066	<MDL	<MDL	0.0890
M10	1.3854	0.1926	0.0430	<MDL	<MDL	0.1992
M11	0.3648	1.1813	0.5247	<MDL	<MDL	0.2740
M12	<MDL	0.3049	0.1326	<MDL	<MDL	0.0939
M13	<MDL	0.5936	0.1559	<MDL	<MDL	0.1033

MDL = Method detection limit

Table B-10. Environmental parameters for PBDE and MeO-BDE (pg/m^3) MOUDI sampling. Meteorological parameters are reported as the mean ± std. deviation.

Sampling Date	∑PBDE	∑MeO-BDE	$PM_{2.5}$ ($\mu g/m^3$)*	Temperature (°C)Ŧ	Wind Speed (km/hr)Ŧ
July 28, 2015 - Aug. 24, 2015	2.10	2.39	10.46 ± 4.50	17.33 ± 4.40	22.10 ± 8.00
Aug. 24, 2015 - Oct. 8, 2015	0.78	0.24	8.56 ± 3.87	12.80 ± 4.50	21.00 ± 8.60
Jan. 27, 2016 - Feb. 29, 2016	0.28	2.19	5.75 ± 3.96	-1.70 ± 5.10	28.12 ± 12.90
May 31, 2016 - June 29, 2016	1.35	0.06	5.92 ± 3.54	10.70 ± 6.20	22.30 ± 9.50
June 30, 2016 - Aug. 1, 2016	2.36	0.06	5.61 ± 4.28	15.40 ± 5.20	21.10 ± 9.50
Aug. 2, 2016 - Sept. 7, 2016	1.59	0.06	6.33 ± 3.62	16.10 ± 3.60	22.50 ± 9.40
Sept. 9, 2016 - Oct. 7, 2016	2.41	0.18	6.68 ± 3.46	11.00 ± 4.10	24.40 ± 9.80

* National Air Pollution Surveillance (NAPS)

Ŧ St. John's International Airport

Appendix C Supporting Information for Chapter 5

C.1 Fish analysis method detection limit

A gas chromatography mass spectroscopy (GC-MS) run of ~27 min per sample (including automated solvent syringe cleaning and sample transfer) for a continuous GC-MS analysis of about 20 to 100 samples, including solvent blanks and internal standard calibration, could operate for a few hours to about a day. All fish samples were randomly quantified with 3 different calibration curves to prevent systematic bias and monitor instrumental stability during these long GC-MS runs. The sample method detection limit (Table C-1) was calculated with the method blank from the accelerated solvent extraction (ASE). ASE samples were also processed randomly.

Table C-1. Method detection limit (MDL, ng/g) of Atlantic cod and Greenland halibut liver samples.

Blank	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47
A	0	2.08	0.38	0.04	0	0	0
B	0	0	0	0	0	0	0
C	2.01	2.58	0	0.63	0	3.02	0
D	2.92	5.39	1.77	0	0	1.74	0
E	3.38	0	0	2.70	0	0	0
F	0	0	0	0	0	0	0
G	0.25	0.92	0	0.30	0.57	0	0

Table C-2. Anthropogenic PBDE and MeO-BDE levels (ng/g) in 2014 Atlantic cod fish livers from the Gulf of St. Lawrence (GSL).

Fish Sample	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47	Depth (m)	Latitude	Longitude
A	4.48	33.6	17.0	3.88	3.12	13.7	22.73	107.5	48.91	-59.35
B	1.90	38.5	31.4	1.87	<MDL	23.6	30.41	119.3	48.99	-59.31
C	8.20	21.4	32.7	0.42	<MDL	11.0	5.87	199.5	49.30	-59.23
D	<MDL	13.9	10.1	1.26	<MDL	8.89	7.66	50.5	48.80	-59.10
E	<MDL	8.0	<MDL	<MDL	<MDL	2.56	2.39	74.5	49.11	-58.73
F	2.68	8.5	0.2	10.7	<MDL	7.74	6.81	92.8	49.26	-58.68
G	<MDL	7.0	0.5	<MDL	<MDL	17.6	<MDL	101.5	49.56	-58.58
H	1.45	36.3	39.0	<MDL	<MDL	36.1	20.85	85.2	49.26	-58.57
I	0.73	19.2	1.8	0.43	10.5	24.3	4.51	88.9	49.55	-58.39
J	2.81	34.5	48.5	7.77	<MDL	20.1	6.27	69.9	49.96	-57.99
K	1.55	24.6	2.0	1.57	7.37	23.6	14.86	147.0	50.27	-57.73
L	1.18	32.9	1.6	<MDL	0.84	17.4	10.15	122.5	50.46	-57.56
M	0.92	19.0	1.12	4.25	<MDL	9.08	2.64	107.5	50.98	-57.37
N	5.08	22.1	38.8	<MDL	<MDL	14.1	16.01	119.3	51.58	-56.61
Range	0.73-8.20	6.97-38.5	0.24-48.5	0.43-10.7	0.84-10.5	2.56-36.1	2.39-30.4	50.5-199.5		
Average	2.21 ± 2.33	22.8 ± 11.0	16.1 ± 18.0	2.30 ± 3.31	1.56 ± 3.2	16.4 ± 8.71	10.8 ± 8.93			

MDL = Method detection limit

Table C-3. Anthropogenic PBDE and MeO-BDE levels (ng/g) in 1993 Atlantic cod fish livers from the Gulf of St. Lawrence (GSL).

Fish Sample	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47	Depth (m)	Latitude	Longitude
A	3.95	71.0	25.0	<MDL	<MDL	32.6	<MDL	97.7	48.37	-59.39
B	18.9	79.5	40.1	<MDL	<MDL	61.9	9.63	5	50.38	-57.53
C	4.32	57.0	<MDL	<MDL	<MDL	32.5	<MDL	150	50.33	-57.32
Range	3.95-18.9	57.0-79.5	25.0-40.1			32.5-61.9	9.63	5-150		
Average	9.04 ± 8.5	69.2 ± 11.4	21.7 ± 20.3			42.3 ± 16.9	3.21 ± 5.56			

MDL = Method detection limit

Table C-4. Anthropogenic PBDE and MeO-BDE levels (ng/g) in 2014 Atlantic cod fish livers from the Gulf of St. Lawrence outflow (GLO).

Fish Sample	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47	Depth (m)	Latitude	Longitude
2014, GLO	1.52	6.72	<MDL	0.12	<MDL	9.44	2.67	59.8	55.61	-55.61
2014, GLO	3.64	29.9	50.2	<MDL	<MDL	41.0	22.5	161.7	56.57	-56.57
2014, GLO	<MDL	1.98	<MDL	<MDL	<MDL	3.38	<MDL	108.3	56.05	-56.05
2014, EC	<MDL	2.17	<MDL	<MDL	<MDL	<MDL	<MDL	149.7	47.13	-54.50
Range	1.52-3.64	1.98-29.9	50.2	0.12		3.38-9.44	2.67-22.5	59.8-232		
Average	1.61 ± 1.51	10.1 ± 12.3	12.7 ± 25.0	10.8 ± 21.4		30.5 ± 30.1	16.4 ± 18.8			

EC = east coast

MDL = Method detection limit

Table C-5. Anthropogenic PBDE and MeO-BDE levels (ng/g) in 2014 Atlantic cod fish livers from the open Atlantic Ocean (AO).

Fish Sample	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47	Depth (m)	Latitude	Longitude
A	1.77	16.1	0.61	0.02	<MDL	21.7	50.6	51.8	49.00	-51.78
B	0.99	7.69	0.67	0.75	12.5	24.4	7.11	292.1	49.91	-51.56
C	2.85	34.5	0.93	18.0	1.80	6.94	27.8	320.4	49.17	-51.40
D	1.48	17.6	1.04	2.21	0.78	9.67	35.0	304.0	49.95	-51.23
E	2.46	7.00	0.02	9.07	<MDL	12.4	12.5	334.8	49.35	-51.06
F	4.23	33.7	10.8	2.82	<MDL	62.1	31.6	302.7	50.33	-50.93
G	1.49	10.2	0.56	6.02	<MDL	10.6	19.8	327.9	50.00	-50.87
H	4.73	22.6	74.4	1.82	<MDL	15.9	30.8	329.1	49.34	-50.71
I	1.64	11.5	0.12	2.95	<MDL	2.54	15.1	275.9	49.09	-50.42
J	5.71	6.11	0.21	5.51	<MDL	34.1	22.6	296.4	49.25	-50.33
K	1.34	9.67	0.25	3.22	<MDL	21.3	23.3	359.2	49.67	-50.20
L	5.02	18.3	0.25	4.01	4.75	22.5	58.9	340.6	48.18	-48.94
M	2.24	3.47	<MDL	<MDL	<MDL	18.4	14.6	312.6	48.07	-48.66
N	2.44	10.1	0.01	3.23	9.37	5.26	13.7	275.9	47.81	-48.07
O	<MDL	1.14	<MDL	8.43	3.31	2.32	<MDL	283.4	47.14	-45.77
P	0.60	0.82	0.06	3.80	2.72	0.13	<MDL	255.1	47.11	-45.53
Range	0.60-5.71	0.82-34.5	0.01-74.4	0.02-18	0.78-12.5	0.13-62.1	7.11-58.9	51.8-359		
Average	2.44 ± 1.66	13.2 ± 10.2	5.62 ± 18.5	3.88 ± 4.46	1.82 ± 3.80	17.50 ± 14.7	23.09 ± 15.8			

MDL = Method detection limit

Table C-6. Anthropogenic PBDE and MeO-BDE levels (ng/g) in 2014 Greenland halibut fish livers from the open Atlantic Ocean (AO).

Fish Sample	BDE-28	BDE-47	BDE-99	BDE-156	BDE-209	MeO-68	MeO-47	Depth (m)	Latitude	Longitude
A	4.95	7.48	1.29	1.91	0	14.3	11.3	324.8	49.00	-51.78
B	0.82	0.53	<MDL	3.76	3.70	2.63	4.11	321	49.168	-51.40
C	0.45	0.71	0.04	6.07	0.77	0.33	1.92	334.8	49.345	-51.06
D	0.19	0.98	1.98	2.43	<MDL	8.34	<MDL	313.6	49.582	-50.95
E	1.43	1.66	<MDL	2.70	3.88	2.89	<MDL	329.2	49.341	-50.71
F	<MDL	<MDL	<MDL	4.18	1.81	<MDL	<MDL	276.7	49.09	-50.42
G	0.10	0.29	<MDL	0.69	0.92	<MDL	<MDL	340.9	48.184	-48.94
H	2.97	16.5	12.5	7.76	1.60	0.29	<MDL	736.0	47.176	-46.56
Range	0.10-4.95	0.29-16.5	0.04-12.5	0.69-7.76	0.77-3.88	0.29-14.3	1.92-11.3	276.7-736		
Average	1.36 ± 1.75	3.52 ± 5.77	1.97 ± 4.31	2.17 ± 2.12	0.56 ± 1.30	5.11 ± 4.73	3.19 ± 3.54			

MDL = Method detection limit